[redacted]

TRANSCRIPT OF RECORD

[redacted]

In the

Supreme Court of the United States

October Term, [redacted]

No. [redacted]105

THE DAVISON CHEMICAL CORPORATION,

Petitioner,

vs.

JOLIET CHEMICALS, INC., AND PLASTICS AND CO-OPANY, JOLIET CHEMICALS, INC., AND [redacted] KEPNER, ELMER,

Respondents.

[redacted]

[redacted]

IN THE

Supreme Court of the United States

OCTOBER TERM, 1949.

No.

THE DAVISON CHEMICAL CORPORATION,
Petitioner,

vs.

JOLIET CHEMICALS, INC., DES PLAINES OIL COMPANY, JOLIET CHEMICALS, LTD., AND KENNETH F. NASH,
Respondent.

ON WRIT OF CERTIORARI TO THE UNITED STATES COURT OF APPEALS FOR THE SEVENTH CIRCUIT.

199199

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In the

United States Court of Appeals

For the Seventh Circuit

No. 9991

THE DAVISON CHEMICAL CORPORATION,
Plaintiff-Appellant,

vs.

JOLIET CHEMICALS, INC., DES PLAINES OIL COMPANY, JOLIET CHEMICALS, LTD., AND KENNETH F. NASH,
Defendants-Appellees.

Appeal from the United States District Court for the Northern District of Illinois, Eastern Division.

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1 Pleas had at a regular term of the United States District Court for the Eastern Division of the Northern District of Illinois begun and held in the United States Court Rooms in the City of Chicago, in the Division and District aforesaid on the first Monday of June (it being the 6th day thereof) in the Year of Our Lord One Thousand Nine Hundred Forty-nine and of the Independence of the United States of America, the 173rd Year.

Present:

Honorable John P. Barnes, District Judge.
Honorable Philip L. Sullivan, District Judge.
Honorable Michael L. Igoe, District Judge.
Honorable William J. Campbell, District Judge.
Honorable Walter J. La Buy, District Judge.
Honorable Elwyn R. Shaw, District Judge.
Honorable William H. Holly, District Judge.
Roy H. Johnson, Clerk.
Thomas P. O'Donovan, Marshal.

Wednesday: June 29th, 1949.

Court met pursuant to adjournment.

Present: Honorable Elwyn R. Shaw, Trial Judge.

2 Pleas had at a regular term of the United States District Court for the Eastern Division of the Northern District of Illinois begun and held in the United States Court Rooms in the City of Chicago, in the Division and District aforesaid on the first Monday of July (it being the 4th day thereof) in the Year of Our Lord One Thousand Nine Hundred Forty-Nine and of the Independence of the United States of America, the 174th Year.

Present:

Honorable John P. Barnes, District Judge.
Honorable Philip L. Sullivan, District Judge.
Honorable Michael L. Igoe, District Judge.
Honorable William J. Campbell, District Judge.
Honorable Walter J. La Buy, District Judge.
Honorable Elwyn R. Shaw, District Judge.
Honorable William H. Holly, District Judge.
Roy H. Johnson, Clerk.
Thomas P. O'Donovan, Marshal.

Tuesday: July 26th, 1949.

Court met pursuant to adjournment.

Present: Walter J. La Buy, Trial Judge.

3 UNITED STATES DISTRICT COURT

Northern District of Illinois,

Eastern Division.

The Davison Chemical Corporation, a corporation, *Plaintiff*, *vs.* Joliet Chemicals, Inc., a corporation, DesPlaines Oil Company, a corporation, Joliet Chemicals, Ltd., a partnership, and Kenneth F. Nash, *Defendants.*	Civil Action No. 47 C 1098.

AGREED STATEMENT OF CASE UNDER RULE 76.

The parties to this case, by their attorneys, present the following statement of the case in the above entitled case:

The Davison Chemical Corporation, a corporation, filed its complaint herein on July 29, 1947, claiming that it is a corporation organized and existing under the laws of the State of Maryland and having its principal place of business at Baltimore, Maryland, and made its principal place of business at Baltimore, Maryland, and made defendants Joliet Chemicals, Inc., a corporation organized and existing under the laws of the State of Delaware, DesPlaines Oil Company, Inc., a corporation organized and existing under the laws of the State of Illinois, Joliet Chemicals, Ltd., a partnership, formed under the laws of Illinois, and Kenneth F. Nash, a resident and inhabitant of Will County, Illinois, and of the Northern District of Illinois, Eastern Division.

4 The complaint alleged acts of infringement described in the complaint took place at Joliet, Illinois, at which city each defendant had its principal place of business. The complaint stated jurisdiction on the basis that the suit was in equity under the patent laws of the United States.

The complaint set forth three patents which defendants were accused of infringing, two of which were withdrawn. The suit was therefore limited to letters patent of the United States, No. 1,900,859, issued to Silica Gel Corpora-

tion on March 7, 1933, the inventors, Ernest B. Miller and Gerald C. Connolly, having assigned all their right, title and interest in said invention to said Silica Gel Corporation.

The complaint further alleged present ownership of the patents in plaintiff by assignment on or about December 31, 1935, from the then owner of the patent. The complaint claims that from May 12, 1944, to date the defendants manufactured and sold silica gels in accordance with the processes and embodying the inventions of the said letters patent and in infringement thereof and that plaintiff has placed the required statutory notice on all silica gels manufactured by it under said letters patent and has given defendants written notice of their infringement, but that defendants have disregarded said notice and that plaintiff believes that unless the defendants are restrained by process of court, they will continue to infringe said letters patent, and plaintiff thereby will be irreparably injured.

The prayer was for an injunction, accounting of profits for damages and for such further relief as the case may require.

Defendants filed an answer admitting the jurisdictional facts and ownership of the patent by plaintiff as claimed, and set up as defenses, among others, anticipation and cited many patents including among them U. S. letters patent No. 1,297,724 of May 18, 1919, issued to Patrick. Other defenses and a counter-claim charging unfair competition were interposed.

On June 1, 1949, the court entered an order ordering that in accordance with the provisions of Rule 42 (b) issues presented by the counter-claim be separated for trial from the issues presented by the complaint. It was further ordered that without prejudice to any other claims or defenses presented by the complaint, answer, counter-claim and reply to the counter-claim, a separate hearing on a Motion for Summary Judgment filed my defendants be had on June 28, 1949.

On June 3, 1949, defendants filed a motion for summary judgment as follows:

"Come now the defendants by their attorneys and move for a summary judgment dismissing the complaint on the ground that the claims in the patent in suit are invalid in view of the Patrick Patent No. 1,297,724 of May 18, 1919.

"In support of their motion defendants will rely solely on disclosure of the Patrick patent, the disclosure of the patent in suit and the file history thereof. There are hence no material facts in issue with respect to this motion."

On June 28, 1949, a hearing was held on defendants' motion for summary judgment. The court reviewed the Connolly et al. patent No. 1,900,859, the Patrick patent No. 1,297,724 of May 18, 1919, the affidavits of J. R. Mecredy and Walter A. Patrick, submitted to the court, the file history of the patent in suit and the deposition of Gerald C. Connolly taken April 16, 1949. Copies of patents No. 1,900,859 and No. 1,297,724 of the affidavits of Mecredy and Patrick, of the deposition of Gerald C. Connolly and of the file history of the patent No. 1,900,859 are attached hereto.

On June 29, 1949, the court entered an order holding that the Connolly et al. patent in suit, No. 1,900,859, is invalid for want of invention and dismissing the complaint, retaining jurisdiction with respect to the issues presented by the counter-claim and as to the matter of costs. A copy
6 of said order is attached hereto.

On July 26, 1949, the court entered an order holding that the Connolly et al. patent No. 1,900,859 is invalid for want of invention, dismissing the complaint herein, entering judgment on the complaint filed herein for defendants and against plaintiff and ordering that plaintiff take nothing by its action herein, the court retaining jurisdiction with respect to the issues presented by the counter-claim and with respect to the costs. A copy of said order is attached hereto.

On July 27, 1949, plaintiff filed its notice of appeal, a copy of which is attached hereto, wherein plaintiff appealed from those parts of the orders of June 29, 1949, and July 26, 1949, wherein the Court held that the Connolly patent in suit No. 1,900,859 is invalid for want of invention, dismissed the complaint, ordered judgment be entered on the complaint for the defendants and against the plaintiff and that plaintiff take nothing by its action herein.

The plaintiff-appellant makes the following statement of points relied upon on appeal:

1. The Court erred in holding Connolly et al. patent No. 1,900,859 invalid for want of invention and in dismissing the complaint.

2. The Court erred in entering a summary judgment herein.

Harold W. Norman,
Attorney for the Davison Chemical Corporation, a corporation, Plaintiff-Appellant.

Schroeder, Merriam, Hofgren & Brady,
Attorney for Joliet Chemicals, Inc., et al., Defendants-Appellees.

The foregoing Agreed Statement of Case Under Rule 76 is hereby approved this 4th day of August, 1949.

Enter:

Igoe,
Judge.

HISTORY OF

THE APPLICATION WHICH RESULTED IN PATENT TO G. C. CONNOLLY ET AL, DATED MAR 7, 1933 PATENT NO. 1,900,859

References:

1,297,724 Patrick
1,665,264 Holmes et al

Page 342, Hodgman et al—Handbook of Chemistry and Physics, pub. in 1922 by Chemical Rubber Publishing Co., Cleveland, Ohio.

8 1930

Serial Number
470,761

Div. ~~56~~ 59
Patnt No. 1,900,859
Method of Making Gels

Gerald C. Connolly and Ernest B. Miller,
of Baltimore Maryland.
Assors. to The Silica Gel Corporation,
of Baltimore, Md., a corp. of Maryland.

Application filed complete July 25, 1930

Examined and passed for Issue Aug. 9, 1932
V. I. Richards, Exr. Div. 59

Notice of Allowance Aug. 9, 1932

Final Fee $30 Feb. 9, 1933

Dated March 7, 1933

Attorney: Watson, Coit, Morse & Grindle,
~~*Mather Bldg.,*~~ 815—15th St., N.W.,
Washington, D. C.

(Cl. 23-182)

CONTENTS:

1. Application papers
2. Rejection Apr. 7, 1931
3. Letter Oct. 7, 1931
4. Letter & Oath Oct. 15, 1931
5. Chge. of Add. Nov. 7, 1931
6. Rejection Apr. 4, 1932
7. Amendt. A May 28, 1932
8. Amendt. B July 28, 1932
9. Notice of Suit Aug. 1, 1947

SEARCH NOTES:

Class 23, Sub. 182 Apr. 1931, L.A.N.

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9 Paper No. 1 July 25, 1930

APPLICATION PAPERS

Petition (giving applicants' post office address as c/o The Silica Gel Corporation, 1800 Baltimore Trust Building, Baltimore, Maryland,) and Power Of Attorney in usual form.

Specification allowed without change.

Original Claims

Can. Per A

~~1. In the process of making gels of different apparent densities, the steps of preparing hydrogels and washing the one to result in the lowest density product with hotter water than the others.~~

~~2. In the process of making gels of different apparent densities, the steps of preparing hydrogels and washing the one to result in the lowest density product with water at 160° to 190° F. and the one to result in a higher density product with water at a lower temperature.~~

~~3. In the process of making gels of different apparent densities, the steps of preparing hydrogels and washing the one to result in the highest apparent density product with water at 90° to 125° F. and the one to result in a lower density product with water at a higher temperature.~~

10

Can. Per A

~~4. In the process of making gels of different apparent densities, the steps of preparing hydrogels, washing one of said hydrogels with water at a temperature~~

~~*ranging from 160° to 190° F. to make a product having a low density, and another with water at a temperature ranging from 90° to 160° F. to make a product having a higher density.*~~

~~*5. In the process of making gels of different apparent densities, the steps of preparing hydrogels, washing one of said hydrogels with water at a temperature ranging from 160° to 190° F. to make a product having a low density, another with water at a temperature ranging from 90° to 125° F. to make a product having a high density, and another with water at a temperature ranging from 125° to 160° F. to make a product having an intermediate density.*~~

~~*6. In the process of making gels having apparent densities ranging from about 0.5 to 0.7 after activation at 600° F., the steps of preparing hydrogels, washing one of said hydro, lo with water at a temperature ranging from 160° to 190° F. to make a product having a density of about 0.5, another with water at a temperature ranging frob 90° to 125° F. to make a product having a density of about 0.7 and another with water at a temper-*~~

11 Can. Per A

~~*ture ranging from 125° to 100° F. to make a product having a density intermediate 0.5 and 0.7.*~~

Add A'>

Oath, in usual form, executed July 24, 1930, before Justine E. Frohnhauser, Notary Public, Baltimore, Md. Foreign applications as follows:

Country	Serial No.	Filed	Patent No.
Argentina	38,761	Mar. 13, 1929	
Australia			18,359/29
Austria	A 8584/28	Dec. 29, 1928	
Belgium			356,949
Canada	344,727	Dec. 20, 1928	
Czechoslovakia	8390/28	Dec. 28, 1928	
Denmark	3,146	Dec. 29, 1928	
Esthonia			1,288
France			652,270
Germany	S 85,275	Apr. 27, 1928	
Great Britain			303,138
Holland	44,279	Dec. 28, 1928	
Italy	182/95	Dec. 29, 1928	
Japan	674	Jan. 24, 1929	
Mexico			29,222
Norway	41,754	Dec. 28, 1928	
Poland	P 25,301	Dec. 29, 1928	
Roumania			16,279
Russia	39,653	Jan. 29, 1929	
Spain			110,759
Sweden	5,605	Dec. 28, 1928	
Switzerland	63,442	Mar. 6, 1929	

Paper No. 2 Apr. 7, 1931

REJECTION

References made of record:

Patrick	1,297,724	Mar. 18, 1919	23-182
Holmes et al	1,665,264	Apr. 10, 1928	23-182

Hodgman et al—Handbook of Chemistry and Physics, published in 1922 by Chemical Rubber Publishing Co. Cleveland Ohio, see page 342.

12 In the oath where patents are listed as granted, the applicant is required to give the filing dates of these patents.

No invention is seen in dissolving various amounts of a substance by varying the temperature of the solvent.

Solubility charts similar to the chart disclosed by Hodgman show that for most salts there will be an increase in amount dissolved with an increase in temperature. The process as disclosed by the applicant is no more than the dissolving of various amounts of inorganic salts from a gel by using a solvent of various temperatures. The gel is a rigid porous silica structure of a fixed volume. The action of washing the gel is the removing of soluble salts from the pores of this structure thus the removing of a definite weight of soluble salts from the gel without changing the actual outside dimensions of the gel. The density is the weight per unit volume. If the volume remains the same, due to its rigid insoluble silica structure, regardless of the amount of washing, the washing removing only the soluble salts carried by the structure and thus decreasing weight of the unit mass, it is obvious, that there will be a decrease in density of the gel due to the washing. To run a series of laboratory washings and determine the density of the gel is not considered invention.

All claims are, therefore, rejected as unpatentable over either Patrick or Holmes et al in view of Hodgman et al.

Patrick and Holmes et al both show the practice of 13 washing the gel.

V. I. Richards,
Examiner.

S.W.G.

Paper No. 3 Oct. 7, 931

LETTER

This amendment is in response to the Official letter of April 7, 1931.

A new oath is being prepared containing the filing dates of all of the foreign patents granted on applications corresponding to the instant application, and same will be forwarded in a few days.

It is noted that the Examiner is of the opinion that washing the hydrogel with hot water does nothing more than remove more of the impurities, and hence because of this more complete removal of impurities the product will have a lower apparent density. This deduction by the Examiner is incorrect for although washing the hydrogel with hot water does not remove the impurities to any appreciable greater degree, yet the product obtained from the hot water washed hydrogel has a very much lower apparent

density than that secured from a cold water washed hydrogel. For eaxmple, if two batches of hydrogel are washed so that the final products have the same residue, one batch being washed with room temperature water and the other with water of 150° F., the hot water washed gel has a decidedly lower apparent density.

A batch of hydrogel was washed for eighty-four hours with wash water at about 80° F., and then dried. The resulting product had a net residue of about 0.02% and an apparent density of 0.72.

Another batch of the same hydrogel was washed for forty-eight hours with water at a temperature of 150° F., and then dried. The resulting product had the same net residue as the other batch, but the apparent density was 0.58.

Here then we have two final products, each having the same net residue, but the cold water washed one having an apparent density of 0.72, compared with a density of 0.58 for the hot water washed one. Expressed in other words the impurities were washed out of both batches of hydrogel to the same extent, and yet the one washed with hot water had a very much lower density.

Again, if different batches of hydrogel are washed with waters at different temperatures for the same length of time, there is a slight decrease in the net residue with increased temperature of wash water, but this decrease is infinitesimal when compared with the decrease in the density. This conclusion is proved by the following:

A hydrogel made in the usual way is dehydrated without any washing whatever. The impurities in the resulting gel are about 40% of the dehydrated gel.

Now take another batch of the same hydrogel and wash it with water at room temperature and then dehydrate. It will be found that the total residue is about 0.51%.

If a batch of the same hydrogel is washed for the same length of time with water at 105° F., the total residue is about 0.23%.

If another batch of the same hydrogel is washed with water at 150°, the total residue is about 0.12%.

Finally, if still another batch of the same hydrogel is washed with water at 175°, the total residue is about 0.12%.

The dehydrated gel obtained from a hydrogal that was not washed had 40% impurities, whereas the products that were washed with water at different temperatures had only

a fraction of 1%. Therefore, the washing removed almost all of the impurities.

If it is thought that the more the impurities removed, the lower should be the density, the following listing of the foregoing results proves the contrary.

Temperature of wash water	Percent of Impurities removed	Density after activation at 600° F.
Room	98.7	0.75
105	99.4	0.696
150	99.4	0.606
175	99.7	0.522

The impurities removed changed about 1%, whereas the density changed 30% of the cold water washed density, or 43% of the 175° water washed density.

Looking at the table from another angle, the impurities removed changed about one part in one hundred, while the density changed about one part in three, that is to say, thirty times as much as the impurities removed changed.

Attached hereto is a graph which shows the infinitesimal change of impurities removed as compared with the great changes in apparent density when the hydrogel is washed with waters at different temperatures. In this graph the width of the rectangles represents the per cent impurities removed, and it will be noticed that all of the rectangles appear to be the same width. On the other hand, the height of the rectangles represents the apparent density, and the change in this respect is clearly shown by this graph.

It is obvious that there is no connection between the
17 change in "impurities removed", on the one hand, and the change in "density" on the other.

The lower density secured with the higher temperature wash water is due to some factor remote from that of "impurities removed". It is thought that the heat itself has something to do with the change in density. For example, the product obtained by merely soaking a hydrogel in hot water for a time and then washing with cold water and drying has a lower density than where the soaking in hot water is omitted.

The present invention goes farther than merely washing out impurities or in producing a low density gel. It includes the following decidedly novel feature:

The density of the product is controlled by the temperature of the wash water.

With wash water of room temperature, a gel of relative higher density is obtained suitable for gas adsorption from dilute mixtures.

With wash water of 175° a low density gel results, most suitable for liquid adsorption work, as in the refining of gasoline, etc.

With a wash water of a temperature intermediate the two above mentioned, say 150°, a gel of a density between the two is secured—suitable for general adsorption work.

18 It is submitted that the foregoing remarks conclusively prove that washing the hydrogel with hot water gives decidedly unexpected and unsuspected results.

The claims are submitted for reconsideration as they are not anticipated by the Patrick or Holmes et al patents taken with the Hodgman solubility table.

The Patrick patent discloses a process for making silica gel by reacting a sodium silicate solution with acid in such proportions and concentrations as to form a sol, allowing the sol to set to a hydrogel or jelly, washing the hydrogel with cold water, and drying it.

Applicants' invention resides in the discovery that the temperature of the water with which the hydrogel is washed controls the apparent density of the product, that is, whether it is a wide or narrow pored gel or has pores of intermediate size. If a dried gel of low apparent density is desired, the hydrogel is washed with water of a temperature between 160° to 190° F., preferably 175° F. for the same length of time as when cold water is desired the hydrogel is washed with water at a temperature between 125° and 160° F., preferably 150° F., for the same length of time as when cold water is used. Where a dried gel of medium apparent density is desired, the hydrogel is

19 washed with water of a temperature of between 90° to 125° F., preferably 105° F., for the same length of time as when cold water is used.

Although a statement appears in the Patrick patent that if the wash water is heated the washing of the gel is facilitated, such statement does not anticipate applicants' invention. This patent is not at all pertinent to applicants' invention because it does not disclose that by washing the hydrogel with water heated to different temperatures it is

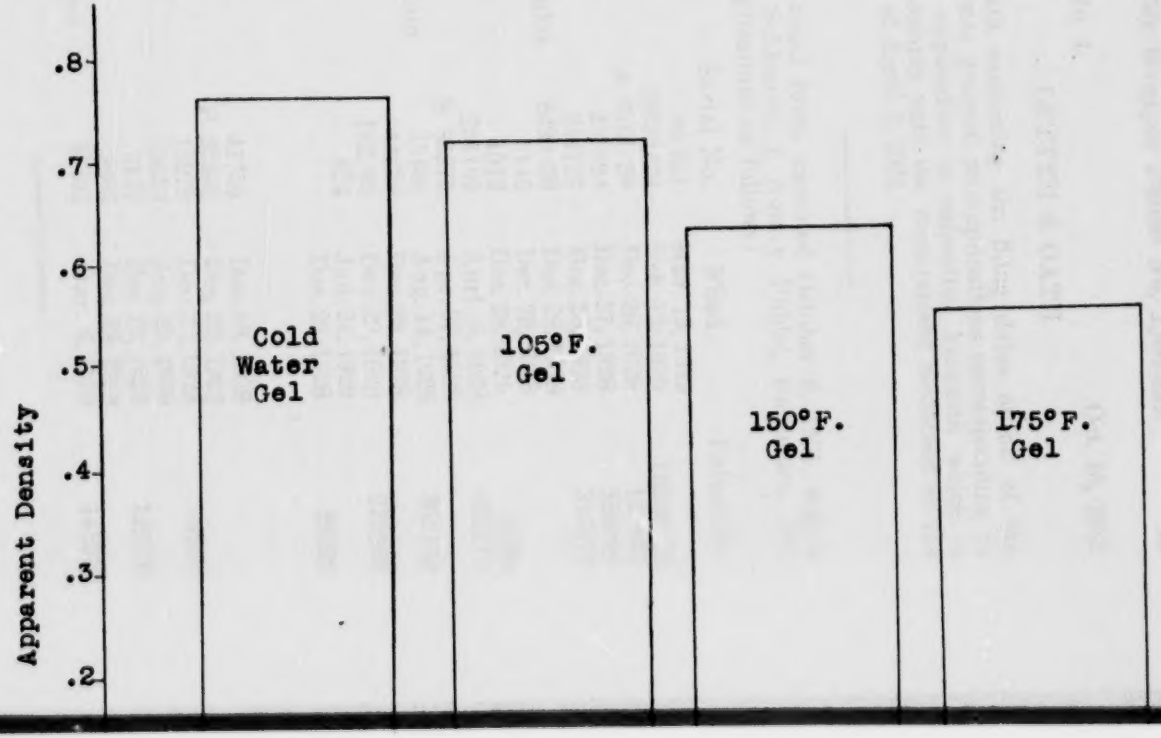
possible to obtain a dried gel of different apparent densities depending upon the temperature of the water used for washing. Neither does such patent teach or even suggest that the temperature of the wash water determines the apparent density of the final dried product.

The Holmes et al patent discloses a process for making silica gel by reacting a sodium silicate solution with a hydrolyzable salt of a heavy metal such as iron chloride to form a gelantinous precipitate, slowly drying the precipitate in an unwashed state at a temperature not much above room temperature until it becomes a hard, solid mass, treating the dried mass with an HCl solution to convert the insoluble ferric oxide into soluble ferric chloride, washing the mass with hot water to remove the ferric chloride, and then drying the mass in the same manner as ordinary silica gel.

In the Holmes et al process the washing of the hard dried material consisting of silicic acid having ferric chloride admixed therewith is for the purpose of removing the ferric chloride and other impurities, and thus increase the number of pores in the hard dried substance. In applicants' process the material which is washed is a soft undried jelly-like mass containing 90% or more of water, commonly termed a hydrogel, and such hydrogel is washed with water heated to a temperature which will give a dried product having the desired apparent density, the washing removing not only the reaction salts to the same degree as when cold water is used but also lowering the density of the dried or dehydrated gel.

The Hodgman solubility table which merely discloses the relative solubilities of a great number of inorganic salts in both hot and cold water is not at all pertinent to applicants' invention because as previously pointed out the invention of this application is not a question of removing more impurities from the gel by using hot water in place of cold water.

From the foreging it is clearly apparent that the Patrick and Holmes et al patents do not even remotely suggest the invention as claimed. Reconsideration and an early allowance is, accordingly, solicited.


Apparent Density
.8
.7
.6
.5
.4
.3
.2
Cold Water Gel
105°F. Gel
150°F. Gel
175°F. Gel

22 Paper No. 4 Oct. 15, 1931

LETTER & OATH

A new oath containing the filing dates of all of the foreign patents granted on applications corresponding to the instant application is submitted herewith which is believed to comply with the requirement contained in the Office letter of April 7, 1931.

Oath, in usual form, executed October 8, 1931, before Justine F. Schleunes, a Notary Public, Baltimore, Md. Foreign applications as follows:

County	Serial No.	Filed	Patent No.
Agentina	38,761	Mar. 13, 1929	
Australia	18359/29	Feb. 12, 1929	18359/29
Austria	A 8584/28	Dec. 29, 1928	120841
Belgium	281398	Dec. 27, 1928	356949
Canada	344727	Dec. 20, 1928	310219
Czechoslovakia	8390/28	Dec. 28, 1928	
Denmark	3146	Dec. 29, 1928	
Esthonia	1512	Dec. 28, 1928	1288
France	254189	Aprl 5, 1928	652270
Germany	S 85275	Apr. 27, 1928	
Great Britain	23460	Aug. 14, 1928	303138
Holland	44279	Dec. 28, 1928	
Italy	182/95	Dec. 29, 1928	275343
Japan	674	Jan. 24, 1929	
Mexico		Dec. 28, 1928	29222
23			
Norway	41754	Dec. 28, 1928	
Poland	P 25301	Dec. 29, 1928	
Roumania	16279	Dec. 30, 1928	16279
Russia	39653	Jan. 29, 1929	
Spain	3457	Dec. 29, 1928	110759
Sweden	5605	Dec. 28, 1928	
Switzerland	63442	Mar. 6, 1929	143377

Paper No. 5 Nov. 7, 1931

CHANGE OF ADDRESS

Please change attorneys' address to—
815 Fifteenth Street, N. W.,
Washington, D. C.

Paper No. 6 Apr. 4, 1932

REJECTION

Responsive to letter filed Oct. 7, 1931.

Applicants' disclosure in this case may be summarized as follows:

After preparation of a hydrogel and breaking it up into pieces, it may be washed with warm water. The temperature of the wash water exerts an influence upon the apparent density of the final product. The temperature range of the wash water is from 90° to 190° F. For convenience or examination or tabulation of results, the experi-
24 ments were recorded in three distinct ranges of temperature:

(a) 90 to 125° Washing for 36-48 hours
(b) 125 to 160° " " " " "
(c) 160 to 190° F " " " " "

The result found was that the highest density and closest pore size were obtained when washing with the lowest temperature water; and conversely the lowest density and largest pore size were obtained with the highest temperature of water.

When washing with water of one temperature, obviously no other temperature was used. Yet the claims attempt to include washing one gel, then another, and still another. This makes the claims actually recite aggregations of as many processes as there are gels treated. While this may appear unduly technical, it is strictly proper. The only way the idea sought to be recited can be properly defined is to develop the relationship which applicant discloses—namely, that the temperature is chosen for the wash water so that he can secure the size of pore structure and the density which has been found to go with that washing treatment.

Stated in another way, this case omits the matter found in prior application 243,762 relating to impurities (salts) removed by washing, but discloses definitely two relationships; namely—as the temperature of the wash water increases (the time being kept constant) the pore size of the resulting gel increases and the density decreases.

No further action on the merits of the present claims can be given; but it would seem that future prosecution could aim to develop the relationship above.

25 Formulation of new claims should take into account the right of the public to use any ordinary range of "heated water" upon the expiration of the Patrick patent in 1936.

The claims are rejected.

V. I. Richards,
Examiner.

G.G.

Paper No. 7 May 28, 1932

AMENDMENT A

In response to the Office action of April 4, 1932, the following amendment is made:

Cancel claims 1-6 inclusive and insert the following claims:

1-2 ~~7-8~~. Claims 1 and 2 of patent without change.

A' 3-4 ~~9-10~~. Claims 3 and 4 of patent with changes indicated.

5. ~~11~~. Claim 5 of patent without change.

Can. Per B ~~12. In the process of producing gels in which hydrogel is washed with heated or cold water, that improvement relating to the control of the apparent densities obtained in the production of a number of gels of different apparent densities which comprises, adjusting the temperature of the wash water at a dif-~~

26

Can. Per B ~~ferent temperature for each gel, the one to result in~~

~~*the lowest density product being washed at the highest temperature.*~~

~~*13. In the process of producing gels in which hydrogel is washed with heated water, that improvement relating to controlling the apparent densities of a number of gels of different apparent densities obtainable from a hydrogel which comprises adjusting the temperature of the wash water at from 160° to 190° F. to make a product having a low density, at from 90° to 125° F. to make a product having a high density, and at 125° to 160° F., to make a product of intermediate density.*~~

A′ 6-9 ~~*14-17.*~~ Claims 6, 7, 8 and 9 of patent with changes indicated.

REMARKS:

Applicants' attorneys wish to express their appreciation for the interviews granted them by the Principal Examiner and the Assistant Examiner in charge of the instant application.

The instant process has, in a prior amendment, been thoroughly distinguished over the Patrick patent of record. As explained in the prior amendment, the washing with heated water, as effected by the instant applicants, effects a reduction in apparent density not because of the removal of impurities but because of the heat of the water itself. As already pointed out, Patrick teaches merely that the use of heated wash water facilitates the removal of impurities.

27

The newly submitted claims are distinct over the Patrick patent in being drawn to the process of controlling the apparent density or to the controlling of the lowering of the apparent density of gels obtained from hydrogels. Each

of the claims are distinct also in expressing the idea that the higher the temperature of the wash water, the lower the apparent density of the gel obtained. Most of the claims admit the washing of hydrogels with heated water to be old.

In Stringham's Book on Patent Soliciting and Examining, Section 132, it is stated that "Art disclosure includes what is necessarily implied, but recognition is usually a necessary element of disclosure". It is believed quite clear that Patrick did not recognize that the use of heated water in the place of cold water would lower the apparent density of the final gel product in a manner and to a degree not attainable by washing with cold water. In this section, the case *Fulton* v. *Bishop,* 284 Fed. 774, was cited in which the court said:

28 "prior accidental production of the same thing, where the character and function were not recognized until the invention of the later patent, does not effect anticipation * * *; and that anticipation is not disclosed by a drawing which only incidentally shows a similar arrangement of parts, where such arrangement is not essential to the first invention, and was not itself adopted and used to perform the function in the second invention, and where the first patent contains no suggestion of the way in which the result sought is accomplished by the second inventor."

It seems clear that any lowering of density which Patrick might have obtained by washing with heated water was accidental. Also it appears obvious that he did not recognize the function of the hot water as used in the present process in lowering the apparent density.

It is well recognized that the use of an old process for a new and non-analogous purpose may be patentable. (See Walker on Patents, 6th Edition, Section 77). In the Patrick process, the heated water is used for the purpose of removing impurities. In the instant process the heated water is used for the new and non-analogous purpose of lowering the apparent density.

Claim 7 is drawn in exact accordance with the form kindly suggested by the Principal Examiner during the above mentioned interview.

29 Claim 8 differs from claim 7 in specifying that the invention pertains to controlling the lowering of the apparent density and that the adjusting of the temperature

of the heated water is adapted to produce a gel of a desired apparent density.

Claim 9 is drawn to controlling the apparent density by treating the hydrogel with heated water and is generic in a sense in that it covers treatment with heated water whether the actual washing be done with heated or cold water.

Claim 10 is specific to controlling the apparent density by soaking the hydrogel in heated water and washing with cold water.

Claim 11 is dependent on claim 10 and specifies the period of the hot water treatment.

Claim 12 is drawn to the control of the apparent densities in the production of a number of gels of different apparent densities.

Claim 13 is similar to claim 12 but is limited to the production of three gels of low, intermediate and high apparent densities.

Claim 14 is also similar to claim 12, but specifies the apparent densities obtained by the adjustment of the temperature of the wash water.

Claims 15, 16 and 17 are species claims under generic claim 14 and cover controlling the apparent densities within three different ranges by the use of wash water within three different ranges.

In view of the fact that the claims now in the case have been put in a form approved by the Principal and Assistant Examiners, it is believed that this application is in condition for an immediate allowance. An early consideration is earnestly requested.

Paper No. 8 July 28, 1932

AMENDMENT B

Supplementing the amendment filed May 28, 1932, the following amendment is made:

Claims 9 and 10 amended as indicated on claims 3 and 4 of Patent; see also Inserts B′ and B².

Cancel claims 12 and 13.

Claims 14, 15, 16 and 17 amended as indicated on claims 6, 7, 8 and 9 of Patent—see Insert B³.

REMARKS:

This amendment is made in an effort to present the claims in the form suggested by the examiner at a recent interview.

Claims 9, 10, 14 to 17, inclusive, as now amended are believed to not only define the invention clearly, but also overcome the objections noted by the examiner at the aforesaid interview.

31 Claim 12 is cancelled because such claim is the substantial equivalent of claim 7.

Claim 13 is cancelled because it is thought that the subject matter of such claim is adequately covered in claims 14 to 17, inclusive.

An early allowance of the application is respectfully requested.

NOTICE OF ALLOWANCE DATED AUGUST 9, 1932

FINAL FEE RECEIVED: FEBRUARY 9, 1933.

Paper No. 9 Aug. 1, 1947

NOTICE OF SUIT

Suit filed in the United States District Court, District of Northern Illinois and Eastern Division, on July 29, 1947, No. 47 C 1098, entitled:

The Davison Chemical Corporation, a corporation
Baltimore, Maryland, Plaintiff,

vs.

Joliet Chemicals, Inc., a corporation et al.,
Joliet, Illinois, Defendant,

brought upon the following patents:

1,772,055	August 5, 1930	Silica Gel Corporation
1,773,273	August 19, 1930	" " "
1,900,859	March 7, 1933	" " "

32 Signed July 30, 1947, at Chicago 4, Illinois.

Roy H. Johnson,
Clerk of said Court.

UNITED STATES PATENT OFFICE

GERALD C. CONNOLLY AND ERNEST B. MILLER, OF BALTIMORE, MARYLAND, ASSIGNORS TO THE SILICA GEL CORPORATION, OF BALTIMORE, MARYLAND, A CORPORATION OF MARYLAND

METHOD OF MAKING GELS

No Drawing. Application filed July 26, 1930, Serial No. 470,761, and in Germany April 27, 1929.

The present invention relates to highly adsorbent gels of varying densities, and methods of preparing the same.

Heretofore in the preparation of adsorbent gels, a hydrogel is made which is washed and then dried.

The principal feature of the present invention is the discovery that the temperature of the wash liquid controls the apparent density of the final product, that is, whether it is a wide or narrow pore gel or has pores of an intermediate size.

Usually, the first or second time that a gel is reactivated by heat, its density is increased, the higher the temperature of activation, the greater the increase in density.

Another feature of the present invention is the discovery that the product is more heat stable if washed with hot water, that is, it will withstand activations at high temperatures with less increase in density.

Other features and objects of novelty will be apparent from the following description.

The steps of the complete process are as follows:

Step 1.—A hydrogel that can be converted into a highly adsorbent gel is prepared in any suitable manner. According to one well-known method, in order to secure a silica hydrogel, silicate and acid solutions are mixed with violent agitation in such proportions and concentrations as to give a solution termed "sol", having an acidity of 0.1 N. to 0.9 N., preferably 0.5 N. Thus, if silicate and acid solutions of equal volumes are employed, a 25° Bé. solution of sodium silicate may be taken and a 21.5° Bé. sulphuric acid solution. The sodium silicate employed contains about 4.6% available Na_2O and 16.35% available SiO_2. The sulphuric acid solution employed contains about 23.25% available H_2SO_4. The vigorous agitation is required in order to maintain all parts of the solution acid. If the ingredients are taken in concentrations and proportions such that the excess of the acid in the solution is very small, say less than 0.1 N., the tendency of the ingredients to react and form a precipitate can be retarded by cooling the ingredients either before or at the time of mixing.

Step 2.—The solution, or "sol", is allowed to stand, and its viscosity gradually increases until after a few hours the whole body of the sol hardens and spontaneously sets or coagulates into a homogeneous mass termed the "hydrogel". This setting of the sol is preferably carried out at a temperature of about 70° F. The time of setting is approximately 5 hours. If such a hydrogel is properly washed and almost wholly dehydrated, a hard, porous, highly adsorbent gel will result.

It is to be understood that the invention is not limited to this particular manner of producing the hydrogel, as other methods may be employed.

Step 3.—The hydrogel is then allowed to stand for about 2 hours longer or a total of 7 hours from beginning of mixing, and thereafter is broken up and placed upon suitable trays.

Step 4.—The hydrogel is washed from 36 to 48 hours with water at the proper temperature to give a final product of the desired apparent density. If a high density product is wanted, that is, a close pore gel suitable for adsorption in the gaseous and vapor phase, the hydrogel is washed 36 to 48 hours with water at a temperature of 90° to 125° F. but preferably in the neighborhood of 105° F. This will give a final dried product having apparent densities of about 0.69, 0.91 and 1.24 after reactivations for three hours at temperatures of 600°, 1,000° and 1,600° F. respectively.

If a final product with a somewhat lower density is wanted, a product suitable for general adsorption work, the hydrogel is washed from 36 to 48 hours with water at a temperature of 125° to 160° F., preferably about 150° F. The final dried product has apparent densities of about 0.61, 0.79 and 0.99 after reactivations for three hours at temperatures of 600°, 1,000° and 1,600° F., respectively.

For a low density or wide pore gel, suitable for liquid phase adsorption and adsorption from vapor saturated gas mixtures, the hy-

drogel is washed from 36 to 48 hours with water at a temperature of 160° to 190° F. but preferably at about 175° F. The final dried product has apparent densities of about 0.52, 0.64 and 0.79 after reactivations for three hours at temperatures of 600°, 1,000° and 1,600° F.

Alternative step 4.—According to another method, the hydrogel is soaked for six hours or more in water having a temperature of 105° to 175° F., or is washed for the same length of time with water of this temperature. Thereafter the hydrogel is washed with cold water below 70° F. for about 45 hours. The final product will have an apparent density depending upon the temperature of the hot water.

Step 5.—After the hot water treatment, the hydrogel is dried or dehydrated in any suitable manner. According to one method, this is accomplished by passing a stream of air over the hydrogel at a temperature of 75° C. to 120° C. for a time and then slowly increasing this temperature to 300° C. to 400° C. Other methods giving a satisfactory product may be employed. The final product usually has a water content of 5% to 15% of the weight of the dried gel and may have an apparent density as low as about 0.5.

The term "apparent density" as used herein is the weight in grams of one cubic centimeter of the material made up of particles of a definite size. The figures given herein for the value of the apparent density after activation at 600° F. were obtained from a mass of gel of 8 to 14 mesh particles, that is to say, all the particles will pass through an 8-mesh sieve, but will be caught on a 14-mesh sieve. The values for apparent density after activation at 1.000° to 1.600° F. were obtained with samples of the gel in powdered form of 200 to 300 mesh, that is to say, the particles of the gel will pass through a 200-mesh sieve but will be caught on a 300-mesh sieve.

This application is a continuation in part of application Serial No. 248,762, filed December 30, 1927.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. In the process of producing gels in which a hydrogel is washed with heated water, that improvement pertaining to controlling the apparent density of the gel which comprises adjusting the temperature of the heated water, the temperature chosen for the water being the higher as the apparent density desired is lower.

2. In the process of producing gels in which a hydrogel is washed with heated water for the removal of impurities, that improvement pertaining to the lowering of the apparent density of the final gel obtained which comprises, adjusting the temperature of the heated water to that adapted to produce a gel of the desired apparent density, the higher the temperature of said wash water the lower the apparent density of the final dried gel obtained.

3. In the process of producing gels in which a hydrogel is washed with heated water, that improvement relating to controlling the apparent density which comprises, adjusting the temperature of heated water to that adapted to produce a gel of the desired apparent density, and treating the hydrogel therewith, the temperature chosen for the water being the higher as the apparent density desired is lower.

4. In the process of producing gels, that improvement relating to controlling the apparent density which comprises soaking the hydrogel in heated water, the temperature of which has been adjusted to produce the gel of the desired apparent density, the temperature chosen for the water being the higher as the apparent density desired is lower, and washing the treated hydrogel with cold water.

5. A process according to claim 4 wherein said soaking in heated water is for a period of about six hours.

6. In the process of producing gels in which a hydrogel is washed with heated water, that improvement relating to controlling the apparent density of the gel within the range of about 0.5 to 1.24 when activated at about 600° to 1600° F. which comprises adjusting the temperature of the wash water within the range of from about 90° to 190° F., the temperature chosen for the water being the higher as the apparent density desired is lower.

7. In the process of producing gels in which a hydrogel is washed with heated water, that improvement relating to controlling the apparent density of the gel within the range of about 0.52 to 0.79 when activated at about 600° to 1600° F. which comprises, adjusting the temperature of the wash water within the range of about 160° to 190° F., the temperature chosen for the water being the higher as the apparent density desired is lower.

8. In the process of producing gels in which a hydrogel is washed with heated water, that improvement relating to controlling the apparent density of the gel within the range of about 0.61 to 0.99 when activated at about 600° to 1600° F. which comprises, adjusting the temperature of the wash water within the range of about 125° to 160° F., the temperature chosen for the water being the higher as the apparent density desired is lower.

9. In the process of producing gels in which a hydrogel is washed with heated water, that improvement relating to controlling the apparent density of the gel within the

range of about 0.69 to 1.24 when activated at about 600° to 1600° F. which comprises, adjusting the temperature of the wash water within the range of about 90° to 125° F., the temperature chosen for the water being the higher as the apparent density desired is lower.

In testimony whereof we hereunto affix our signatures.

GERALD C. CONNOLLY.
ERNEST B. MILLER.

UNITED STATES PATENT OFFICE.

WALTER A. PATRICK, OF BALTIMORE, MARYLAND.

SILICA GEL AND PROCESS OF MAKING SAME.

1,297,724. Specification of Letters Patent. Patented Mar. 18, 1919.

No Drawing. Application filed December 7, 1915. Serial No. 65,761.

To all whom it may concern:

Be it known that I, WALTER A. PATRICK, a citizen of the United States, residing in Baltimore, Maryland, have invented certain new and useful Improvements in Silica Gels and Processes of Making Same, of which the following is a specification.

This invention has reference to novel adsorbent materials and to novel methods of producing these adsorbents.

It is a special object of my invention to produce highly porous gels of silica possessing great adsorbing powers. A further object of my invention is to eliminate the objections and uncertainties in the present methods of preparing silica gels and to carry out the process in a simple and efficient manner which yields a uniform product.

Another object of my invention is to produce a highly porous, hard silica gel and which when the water content is greatly reduced will be transparent and have a glassy appearance.

A still further object of my invention is to improve the method of drying the precipitated silica gel so as to produce a gel which shall be stable at high temperatures.

Silica gel has been prepared by mixing solutions of sodium silicate or water-glass with acid solutions. A large excess of acid was used in order to prevent the mixture from setting in the process of mixing, because gel formed by rapid setting when acid is added to water-glass has been found worthless as an adsorbent. In order to get the mixture to set it was then found necessary to remove the excess acid and the salt formed in the reaction. This is invariably done by dialysis, a process which is very slow and furthermore wasteful of silicic acid, because the colloidal silicic acid passes through the dialyzing membrane at the beginning of the dialysis. In my improved process, I produce silica gel of excellent quality by avoiding the impractical and cumbersome step of dialysis.

I carefully determine the concentrations of acid and water-glass solution that when mixed in equal volumes will set to a clear gel within 4 or 5 hours after mixing. Great care must be exercised in bringing the acid and water-glass together, because, owing to the instability of the mixture a rapid coagulation will take place. I prevent this coagulation by efficiently stirring the solutions at the moment of mixing. When HCl is used as the acid a 10% solution (by weight) is employed with a sodium silicate solution having a specific gravity of about 1.185. I obtain good results with water-glass having specific gravities of 1.15 to 1.22. Fairly good results may be obtained with the specific gravity of the water-glass ranging from 1.1 to 1.3. I find that the temperature of the solutions at the time of mixing is an important factor in the time required for the setting of the gel. At a temperature of about 50° C. the mixture sets to a gel in thirty minutes to one hour and the product is just as good as the gel formed by mixing the solutions at a lower temperature but requiring a considerably longer time to set. The preferable temperatures for the solutions at the time of mixing are from 45° to 55° C. but satisfactory results may be obtained at temperatures from 35° to 80° C. On mixing the acid and soluble silicate solution a colloidal solution of silicic acid is first formed. It is from this solution that the silicious compound sets to a gel.

The gel which is formed by allowing the mixture to set is then broken into small pieces and washed free from acid and salt; if the wash water is heated, the washing of the gel is facilitated. The washed gel must now be carefully dried before it can be used. It is essential that the water be removed slowly in the drying operation. I, therefore, first dry the gel in a stream of air at 75° to 120° C. The gel still contains a small quantity of water and is then dried by increasing the temperature slowly up to 300° to 400° C. This produces a most stable substance which can be safely heated to 700° C. without fear of injury.

The method of drying may be modified by taking the material after the first heating at 75° to 120° C., as above described, and subjecting same to a vacuum to remove some more water, the temperature during the vacuum treatment being from 75° to 120° C. The product obtained by this method is just as stable as if the water had been removed by further heating up to 300°–400° C. This gel which is dried in a vacuum is also stable up to 700° C.

The final product is a hard, transparent substance resembling glass very closely in appearance. When prepared in the above manner, it is very porous, the pores being

ultra-microscopic. It is due to this fine porous structure that the gel owes its property of adsorption. Hardness is a desirable property for the gel to possess in order that it may retain its shape and structure and not crumble or pack when placed in a vessel for the adsorption of gas. The danger of getting a compact mass which would offer resistance to the passage of the substance to be adsorbed is thereby eliminated.

Transparency is a function of the size of the pores and water content of the silica gel. When the pores of the gel are filled up with water the pores are large and the gel is transparent. As the water content of the gel is decreased the pores become smaller and the gel loses its transparency up to a certain point. On further reduction of the water content beyond this point the pores continue decreasing in size and the gel begins to recover its transparency; when the water is nearly all eliminated the gel is practically transparent and the pores ultra-microscopic.

In the foregoing example, I described the use of HCl, but any other acid, or mixture of acids, may be used instead. All that is necessary is to regulate the concentration and temperature so that the proper stability of the mixture is attained. Also, other soluble silicates, such as potassium silicate, or mixtures of soluble silicates may be substituted for sodium silicate. The present invention is not limited to the specific details set forth in the foregoing example which should be construed as illustrative and not by way of limitation, and in view of the numerous modifications which may be effected therein without departing from the spirit and scope of my invention, I desire, that only such limitations be imposed as indicated in the appended claims.

In the following claims the word stable in defining the gel is used to mean the property of the gel to retain its characteristics of adsorbing gases and vapors and not undergo chemical change in the presence of air or lose its hardness and transparency.

I claim as my invention:

1. A porous gel stable at temperatures up to 700° C. and having high adsorptive powers.

2. A hard, porous gel, stable at temperatures up to 700° C. and having high adsorptive properties.

3. A hard, porous, transparent gel, stable at temperatures up to 700° C. and having high adsorptive powers, the pores being ultra-microscopic.

4. A porous, glassy silica gel, the pores being ultra-microscopic.

5. A silica gel having ultra-microscopic pores and stable in the presence of air up to 700° C.

6. A hard, transparent silica gel having a cellular structure, glassy appearance, high adsorptive powers and stable at temperatures up to 700° C.

7. A silica gel having a glassy appearance and perforated with exceedingly minute pores, such gel being stable at temperatures up to 700° C. and possessing high adsorptive properties.

8. A process of preparing silica gel, consisting in adding an acid to a soluble silicate solution and thoroughly stirring the substances at the moment of mixing.

9. A process of preparing silica gel comprising adding HCl to a soluble silicate solution in proportion sufficient to set free all of the silicic acid of the silicate and thoroughly stirring the substances at the moment of mixing.

10. A process of preparing silica gel consisting in adding equal volumes of a 10% HCl solution and sodium silicate solution having a specific gravity between 1.15 and 1.22 to each other and thoroughly stirring the same at the moment of mixing.

11. A process of making silica gel comprising adding an acid to a soluble silicate solution, the temperatures of the acid and soluble silicate being between 45° and 55° C. thoroughly stirring the same at the moment of mixing, allowing the gel thus formed to set, washing and then slowly drying said gel.

12. A process of making silica gel comprising adding an acid to a soluble silicate solution, thoroughly stirring the same at the moment of mixing, allowing the gel thus formed to set, washing and then slowly drying said gel.

13. A process of making silica gel comprising adding a 10% HCl solution to an equal volume of sodium silicate solution having a specific gravity between 1.15 and 1.22, thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing and then slowly drying said gel.

14. A process of preparing silica gel comprising adding an acid to a soluble silicate in quantity not less than the equivalent amount of silicic acid to be liberated from the soluble silicate, thoroughly stirring the substances at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C. and then slowly increasing the temperature to a point not exceeding 400° C.

15. A process of preparing silica gel comprising adding an acid to a soluble silicate in quantity not less than the equivalent amount of silicic acid to be liberated from the soluble silicate, thoroughly stirring the substances at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C.

and then slowly increasing the temperature to 300°–400° C.

16. A process of making silica gel comprising adding a 10% solution of HCl to an equal volume of sodium silicate solution of 1.185 specific gravity, thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C. and then slowly increasing the temperature to a point not exceeding 400° C.

17. A process of making silica gel comprising adding a 10% solution of HCl to an equal volume of sodium silicate solution having a specific gravity between 1.1 to 1.3, the temperature of the acid and silicate being between 35° and 80° C., thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C. and then slowly increasing the temperature to 300°–400° C.

18. A process of making silica gel comprising adding a 10% solution of HCl to an equal volume of sodium silicate solution having a specific gravity between 1.15 and 1.22, the temperature of the acid and silicate being between 45° and 55° C., thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C., and then slowly increasing the temperature to 300°–400° C.

19. In a process of making silica gel allowing a colloidal silicious composition to set to a gel, drying the gel in a current of air heated to 75°–120° C., and then slowly increasing the temperature.

20. In a process of making silica gel allowing a colloidal silicious composition to set to a gel, drying the gel in a current of air heated to 75°–120° C., and then slowly increasing the temperature to 300°–400° C.

21. In a process of making silica gel allowing a colloidal silicic acid solution to set to a gel, drying the gel in a current of air heated to 75°–120° C., and then slowly increasing the temperature to a point not exceeding 400° C.

22. In a process of making silica gel allowing a colloidal silicious composition to set to a gel, drying the gel in a current of air heated to 75°–120° C., and then subjecting the gel to a vacuum.

23. In a process of making silica gel allowing a colloidal silicic acid solution to set to a gel, drying the gel in a current of air heated to 75°–120° C., and then subjecting the gel to a vacuum.

24. In a process of making silica gel, allowing a colloidal silicious composition to set to a gel, drying the gel in a current of air heated to 75°–120° C., and then subjecting the gel to a vacuum at a temperature between 75°–120° C.

25. In a process of making silica gel, allowing a colloidal silicious composition to set to a gel, drying the gel in a current of air heated to 75°–120° C., subjecting the gel to a vacuum and then further heating the gel.

26. In a process of making silica gel allowing a colloidal silicious composition to set to a gel, drying the gel in a current of air heated to 75°–120° C., subjecting the gel to a vacuum and then further heating the gel above 120° C.

27. A process of making silica gel comprising adding an acid to a soluble silicate solution, thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing said gel, drying same in a current of air at 75°–120° C., and then subjecting the gel to a vacuum.

28. A process of preparing a hard, transparent, porous silica gel having high adsorptive properties comprising adding a solution of HCl to a solution of sodium silicate in quantity sufficient to set free all of the SiO_2 of the silicate, thoroughly stirring the substances at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C., and then subjecting the gel to a vacuum.

29. A process of making silica gel comprising adding a 10% solution of HCl to an equal volume of sodium silicate solution having a specific gravity between 1.15 and 1.22, the temperature of the acid and silicate being between 45° and 55° C., thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C., and then subjecting the gel to a vacuum.

30. A process of making silica gel comprising adding a 10% solution of HCl to an equal volume of sodium silicate solution of 1.185 specific gravity, the temperature of the acid and silicate being about 50° C., thoroughly stirring same at the moment of mixing, allowing the gel thus formed to set, washing said gel to remove acid and salt, drying the gel in a current of air heated to 75°–120° C., and then subjecting the gel to a vacuum.

WALTER A. PATRICK.

DISCLAIMER

1,297,724.—*Walter A. Patrick*, Baltimore, Md. SILICA GEL AND PROCESS OF MAKING SAME. Patent dated March 18, 1919. Disclaimer filed October 12, 1922, by the assignee, *The Silica Gel Corporation*.

Hereby enters its disclaimer of claims 1 to 7, inclusive, of said patent.

[*Official Gazette November 7, 1922.*]

UNITED STATES PATENT OFFICE.

HARRY N. HOLMES AND JOHN A. ANDERSON, OF OBERLIN, OHIO.

SILICA GELS AND PROCESS OF MAKING THE SAME.

No Drawing. Application filed August 10, 1923. Serial No. 656,716.

This invention relates to silica gels and the process of making the same.

The particular object of the present invention is the production of a silica gel with a greater degree of porosity than such gels heretofore known, with the necessary high gas adsorbtive properties and the additional ability of effectively employing the product for filtration purposes, especially in the filtration of oils for removing therefrom color and offensive odors or impurities in general.

Silica gels have heretofore been prepared by acidifying a proper solution of a suitable silicate, such as water glass, to form a gelatinous mass from which the soluble salt is removed and the water driven off to produce a hard glass-like product containing ultra-microscopic pores, the adsorbing properties of which are well known.

Walter A. Patrick (Canadian Patent No. 217,365, granted March 28, 1922,) also described the production of gels for catalytic purposes, in the production of which he secures the well known ultra-microscopic porous condition in a silica or other gel containing other material with either catalytic or chemical properties, such as an oxide of iron, aluminum, copper, magnesium, cadmium, zinc or manganese, the mixture being prepared for use as a catalyzer or for the production of a chemical effect because of the metallic oxide it contains, which is presented in silica gel form and thereby enhances or makes more active its chemical or catalytic properties because of the large surface presented.

Our invention consists in the production of a silica gel with a higher degree of porosity than other gels heretofore known, by the initial precipitation of a soluble heavily hydrated acidic anhydride, such as hydrated silica, intimately mixed in the act of precipitation with a suitable insoluble metallic oxide, also hydrated, and the subsequent removal of such insoluble metallic oxide after drying this gelatinous precipitate or gel to a rigid solid, thus securing not only the usual ultra-microscopic pores left by the removal of water, and ranging from, say four to ten millimicrons in size, but also an additional number of larger pores ranging in size up to a size just visible with the strongest microscopes, and obtained by the removal of the insoluble metallic oxide. This removal of the insoluble metallic oxide is accomplished by treatment of the dried rigid gel with a suitable acid, or with a base, which reacts chemically with the metallic oxide to convert it into a soluble salt readily washed out with water. This improved process has been carried out in practice as follows:

100 cubic centimeters of sodium silicate solution of 1.375 specific gravity or even as low as 50 cubic centimeters was diluted with 1,000 cubic centimeters of water. With this solution was slowly mixed 150 cubic centimeters of a twice normal solution of ferric chloride. The resulting gel or gelatinous precipitate was dried slowly at a temperature not much above room temperature until it became a hard solid, whereupon it was treated with a six normal solution of hydrochloric acid to convert the insoluble ferric oxide resulting from the reaction between the ferric chloride and sodium silicate into soluble ferric chloride. The ferric chloride and other soluble compounds formed in the reactions were then washed out with water, the ferric chloride being recovered for further use, if desired. Preferably the water should be hot, and if the dried gel is steamed just before its treatment with acid it is less likely to be broken into small lumps. The product, washed clear of the soluble chlorides, is again dried to its final form in the same manner as ordinary silica gel, and is a hard mass. The invention is not limited to the use of ferric chloride as described in the illustration for other soluble iron salts may be used or a soluble nickel salt or, in fact a solution of any metallic salt which when mixed with a soluble silicate yields a gel or a gelatinous precipitate. The intimacy of mixture thus secured is far superior to that secured by mere stirring in of some insoluble oxide while a silica gel is setting.

A silica gel, prepared in the manner described, especially with the greater quantity (100 cubic centimeters) of silicate, is very highly selectively adsorbent towards certain gases. In addition, such gels may be successfully used in filtration processes. For example, the gel prepared with 50 cubic centimeters of silicate not only is highly adsorbent but has also been used for the filtration of a rank petroleum oil, chosen for the purpose because it contains considerable sulphur and is difficult to refine. The sample of our silica gel was utilized to filter this petroleum oil in parallel with another silica gel prepared by the older process of addition of an acid to water glass and washing and drying the gel

product. It was found that the filtrate comes through our gel much more rapidly than through the ordinary gel. Our filtrate at first was as clear as kerosene and nearly free of sulphur odor, being followed by other filtrate having the usual clear, rich colors of lubricating oil, after which the filtrate became darker and darker. The filtrate coming through the ordinary gel sample was practically black from the start, and in this case the removal of sulphur was not quite so marked as when our gel was used.

Obviously other soluble silicates than sodium silicate may be used. Indeed, as described in the Canadian Patrick patent, above mentioned, other substances than silicates may be used. Moreover, any suitable metallic oxides or bases may be used which are capable of being formed intimately mixed in the silica gel and removed therefrom by subsequent conversion into soluble compounds which are then washed out so as to leave a very highly porous gel.

The product is useful in many ways, not only for its ability to absorb gases but also because of its ability to separate compounds in the act of filtration.

What we claim is:

1. The process of preparing hard silica gel with great porosity, comprising mixing a soluble silicate solution with a solution of a metallic salt to form hydrated silica, a soluble salt, and an insoluble metallic oxide, drying in a manner to produce and preserve in a rigid structure and without material shrinkage the usual ultra-microscopic pores, adding an acid to convert the insoluble metallic oxide into a soluble metallic salt, and washing out soluble metallic and other salts, thereby producing additional pores and increasing the total porosity.

2. The process of preparing hard silica gel with great porosity, comprising mixing a soluble silicate solution with an excess solution of an iron salt to form hydated silica, a soluble salt, and iron oxide, drying in a manner to produce and preserve in a rigid structure and without material shrinkage the usual ultra-microscopic pores, treating with an acid to dissolve the iron oxide, and washing out the now soluble salts, thereby producing additional pores and increasing the total porosity.

3. The process of preparing silica gel, comprising deliberately mixing a soluble silicate solution with a material quantity of metallic chloride solution to form insoluble hydrated silica and a metallic oxide, dissolving out the metallic oxide by chemical reaction after drying to the form of a comparatively firm solid, and subsequently washing with water.

4. The process of increasing the porosity of inorganic gels, comprising precipitating a gel containing some material capable of conversion to soluble form by a given reagent and other material incapable of such conversion by the same reagent, treating said gel in a manner to produce the usual ultra-microscopic pores and to set and preserve the structure without subsequent material shrinkage of the pore walls, subsequently treating such gel with said reagent to thereby convert the first named material to water soluble form, and washing out the solution thereof, to thereby produce additional pores and increase the total porosity.

5. The process of preparing hard silica gel with great porosity, comprising deliberately mixing a solution of of soluble silicate and a material quantity of a substance forming therewith insoluble basic material, drying in a manner to produce and preserve in a rigid structure and without material shrinkage the usual ultra-microscopic pores, subsequently converting the insoluble basic material into a water soluble compound readily dissolved out, and then washing to remove said water soluble compound.

6. The process of preparing hard silica gel with great porosity, comprising deliberately mixing a solution of soluble silicate and an excess of a substance forming therewith insoluble metallic oxide and hydrated silica, drying in a manner to produce and preserve in a rigid structure and without material shrinkage the usual ultra-microscopic pores, subsequently converting the insoluble metallic oxide into a water soluble compound readily dissolved out, and then washing to remove said water soluble compound.

7. A process of preparing a hydrated inorganic gel, consisting in mixing a water solution of a soluble salt of an acid, whose anhydride can be heavily hydrated and is insoluble, with a readily hydrolizable salt of a metal to form a gel of intimately mixed insoluble hydrated metallic oxide and an insoluble heavily hydrated acidic anhydride, treating said gel in a manner to produce the usual ultra-microscopic pores and to set and preserve the form of the structure without subsequent material shrinkage of the pore walls, and removing the metallic oxide by its conversion into a water soluble compound by reaction with a suitable reagent and subsequent washing out of the soluble compound.

In testimony whereof we hereby affix our signatures.

HARRY N. HOLMES.
JOHN A. ANDERSON.

PAGE UPSIDE DOWN IN BOOK

SOLUBILITY OF INORGANIC SALTS IN WATER

The table shows the number of grams of the substance indicated by the formula at the side which can be dissolved in 100 grams of water at the temperature in degrees Centigrade given at the top.

Substance.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
$AgNO_3$	115 0	160 0	215 0	270 0	335 0	400 0	470 0	550 0	650 0	780 0	910 0
$Al_2(SO_4)_3$	31 2	33 5	36 2	40 4	45 7	52 1	59 1	66 2	73 1	80.8	89 1
$Al_2K_2(SO_4)_4$	3 0			5 4			24 5				154.0
$Al_2(NH_4)_2(SO_4)_4$	2 6	4 5	6 6	9 1	12 4	15 9	21 1	27.0	35 2		
BaO_2	1 1	1 5	2 2		4 0	?	6 2		9 5		15 7
$BaCl_2$	31 6	33 3	35 7	38 2	40 8	43 6	46 4	49 4	52 4	55 6	58 8
$Ba(NO_3)_2$	5 0	7 0	9 2	11 6	14 2	17 1	20 3	23 6	27 0	30 6	34 2
$Ba(OH)_2.8H_2O$	1 7	2 5	3 9		8 2		20 9		101 4		
$CaCl_2$	59 5	65 0	74 5	101 0	115 3		136 8	141 7	147 0	152.7	159 0
$Ca(OH)_2$	0 185	0 176	0 165		0 141		0 116		0 094		0 077
$CdSO_4.\frac{8}{3}H_2O$	76 5	76 0	76 8		78 5		83 7	Becomes H_2O	CdSO at	$_4$ 74°	
$CoCl_2$	40 5	44 0	50 0	56 5	65 0	93 5	94 0	96 0	98 0		103 0
$CsCl$	161 4	174 4	186 5	197 3	208 0	218 5	229 0	239 5	250 0	260.1	270 5
$CaNO_3$	9 3	14 9	23 0	33 9	47 2	64 4	83 8	107 0	134 0	163 0	197 0
$CaSO_4$	167 1	173 1	178 7	184 1	189 9	194 9	199 9	205 0	210 3	214 9	220 3
$Cu(NO_3)_2$	81 8		125 0		159 8		179 1		207 8		
$CuSO_4$	14 9		20 0	25 5	29 6	33 6	39 0	45 7	53 5	62 7	73 5
$FeCl_2$			68 5			82 0			104 0	105 0	106 0
$FeCl_3$	74 4	81 9	91 8			315 1			525 8		535 7
$FeSO_4$	15 6	20 8	26 4	33 0	40 2	48 6	55 0	56 0	50 0	43 0	
H_3BO_3	1 0	2 5	4 0	5 5	7 0	9 0	11 0	13 0	17.0	22 0	27.5
$HgCl_2$	4 3	6 6	7 4	8 4	9 6	11 3	13 9	17.3	24 3	37.1	54.0
KBr	54 0		66 0		78 0		86 0		96 5		105 0
K_2CO_3	105 0			114 0	117 0	121 0	127 0	133 0	140 0	147.0	156.0
KCl	28 5	31 2	34 3	37 3	40 1	42 9	45 8	48 3	51 0	53.8	56.6
$KClO_3$	3 3	5 0	7 1	10 1	14 5	19 7	26 6	32 5	39 6	47.5	56.0
K_2CrO_4	58 9	60 9	62 9	65 0	67 0	69 0	71 0	73 0	75 1	77.1	79.1
$K_2Cr_2O_7$	5.0	8 5	13 1		29 2		50 3		73 0		102.0
$KHCO_3$	22 5	27 7	33 5	39 0	45 2	52 2	60 0				
KI	127 9	136 1	144 3	152 3	160 0	168 0	176 0	184 0	192 0	201.0	209.0
KNO_3	13 3	20 9	31 6	45 8	63 9	85 5	109 9	138 0	169 0	204 0	246 0
KOH	97 0	103 0	112 0	126 0	136 0	140 0	146 0	151.0	158 0	168.0	178 0
K_2PtCl_6	0 7	0 9	1 1	1 4	1 8	2 2	2 6	3 2	3 8	4 5	5 2
K_2SO_4	7 4	9 2	11 1	13 0	14 8	16 5	18 2	19 8	21 4	22 8	24.1
LiOH	12 7	12 7	12 8	12 9	13 0	13 2	12 8	14.4	15 3		17 5
$MgCl_2$	52 8	53 5	54.5		57 5		61 0		66 0		73 0
$MgSO_4.7H_2O$	26 0	30 9	35 6	40 9	46 6						
$MgSO_4.6H_2O$	40 8	42 2	43 9	45 3		50 4	55 0	30.6	64 2	66 9	73 8
NH_4Cl	29 7	33 3	37 2	41 4	46 8	50 4	55.2	60.2	65.6	71.3	77 3
NH_4HCO_3	11 9	15 9	21 0	27 0							
NH_4NO_3	118 3			241 5	297 0				580 0	740 0	871 0
$(NH_4)_2SO_4$	70 6	73 0	75 4	78 0	81 0	84.4	88.0	91.6	96 2	99.2	103.3
NaBr	79.5	84 5	90 3		106 8	116.0	117.0		118 5		120 5
$NaBO_2$		1 6		3 9			10 5	20.0	24 4	31 4	40 8	52.3
$Na_2CO_3.10H_2O$	7 1	12 5	21 4	40 9							
$Na_2CO_3.7H_2O$	20 4	26 3	33 5	43 5	1 H_2O		47.5	46 4	45 5	45 2	45.2
NaCl	35 6	35 7	35 8	36 0	36 3	36 7	37.1	37 5	38 0	38.5	39.1
$NaClO_3$	82 0	89 0	99 0		123 5		147 0		175 0		204 0
Na_2CrO_4	81 7	90.2	90 0		96 0	105 0	115 0		124 0		126 0
$Na_2Cr_2O_7$	163.0	170 0	180 0	197 0	220 0	248.0	263 0	273 0	288 0		433 0
$NaHCO_3$	6 9	8 2	9 6	11 1	12 7	14.5	16 4				
Na_2HPO_4	2 5	3 9	9 3	24 1	53 9			94 9			98 8
NaI	159 0	160 0	179 0	190 0	206 0	225.0	257 0		295 0		302 0
$NaNO_3$	73 0	80 5	88 0	96 2	104 9	114.0	124 0	136 0	148 0	161.0	175.5
NaOH	42 0	51 5	109 0	119 0	129 0	145.0	174 0		313 0		
Na_3PO_4	3 2	3 9	6 2	9 9	13 5	17 4	22 0	25 5	30 0		

SOLUBILITY OF INORGANIC SALTS IN WATER (Cont.)

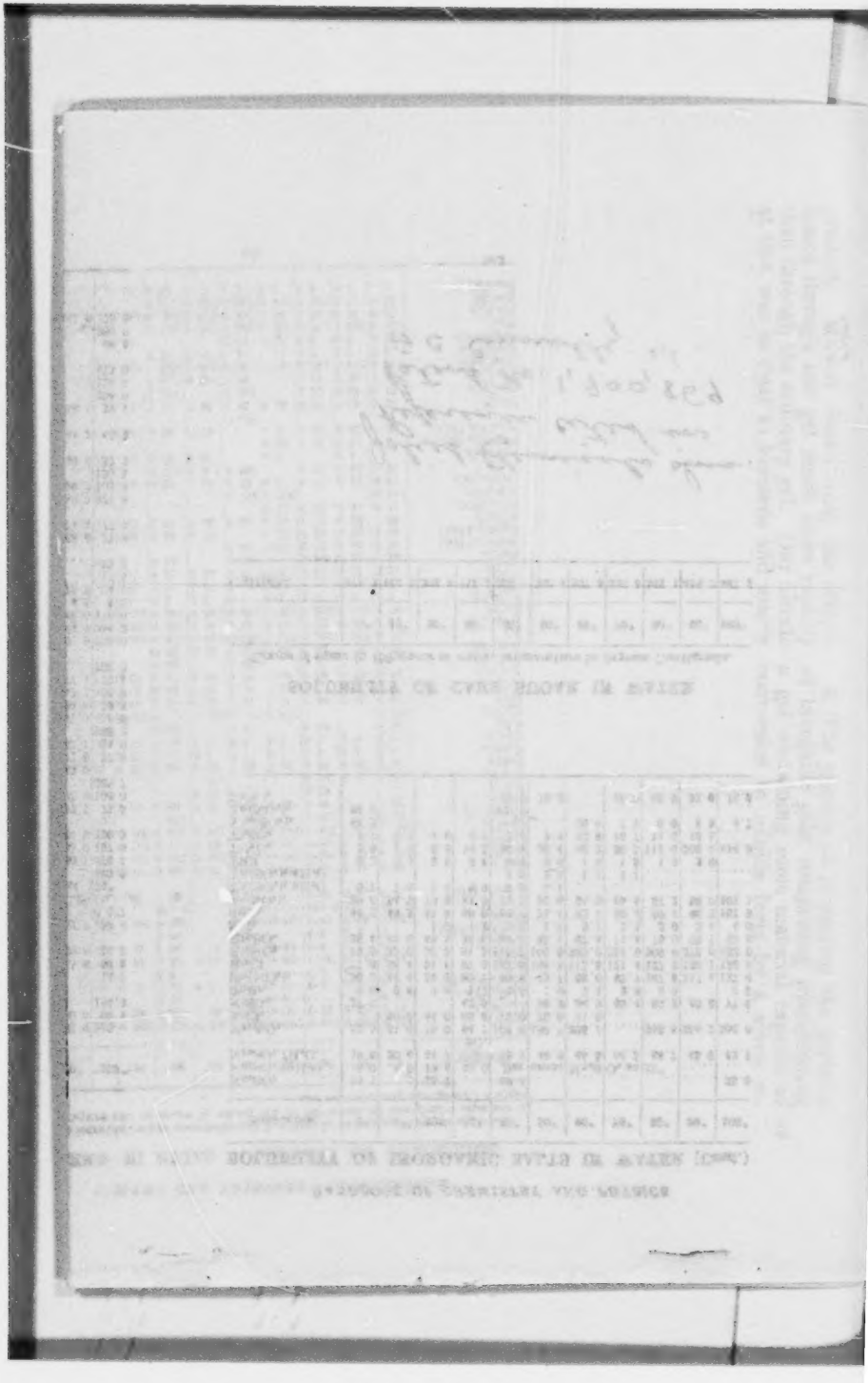
Substance.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Na_2SO_3	14.1		25.7		49 5						33 0
$Na_2SO_3.10H_2O$	3.0	9 0	19.4	40.0	Becomes Na_2SO_3 at		$Na_2S_2O_5$ at	53°			
$Na_2SO_4.7H_2O$	19 6	30.5	44.7	Becomes SO_3	48.8	46.8	44.5	43.7	43.0	43.7	
Na_2SrO_2	52 5	61.0	70 0	84 7	102.6	169.7	208.7		248.8	254.2	266 0
NiCl		60.0	64 0	66 0	73.0	76.0	81.0				
$NiSO_4$	27 2			42.5		60.2	54.8	50.4	46.2	66.8	77.6
PbBr	0.5	0.6	0 8	1.2	1.8	2.9	3 4	3 8	3 3		4.8
$Pb(NO_3)_2$	36 5	44 4	52 3	60.7	69.4	78.7	88.0	97.7	107.6	117 6	127 9
RbCl	77.0	84.4	91.1	97.6	103.5	109.3	115.5	121.4	127 2	133.1	138.9
$RbNO_3$	19 5	33.0	53.2	81.3	116.7	156.6	200.0	251.0	309 0	375.0	453 0
Rb_2SO_4	36 4	42.6	48.2	53.8	58.5	63.1	67.4	71.4	75.0	78.7	81.8
SnI			1.0	1.2	1.4	1.7	2.1	2.5	3.0	3.4	4.0
$SrCl_2$	44 2	48.3	53 9	60 0	66 7	74.4	83.1	89 6	92.4	98 2	101 9
$Sr(NO_3)_2$	39 5	54 9	70 8	87 6	91.2	92.6	94.0	95.6	97.2	99.0	101.1
$Th(SO_4)_2.9H_2O$	0.7	1.0	1 4	2 0	3 0	5.1					
$Th(SO_4)_2.4H_2O$					4 0	2.5	1.6	1.1			
TlCl	0 2	0 2	0 2	0.3	0.6	0.8	1.0	1.3	1.6	2 0	
$TlNO_3$	3 9	6 2	9 6	14 2	20 9	30 4	46.2	69 5	111.0	200.0	416.0
Tl_2SO_4	2 7	3 7	4 9	6.2	7.6	9.2	10 9	12.7	14.6	16 5	
$Yb_2(SO_4)_3$	44 2						10.4	7.2	6.9	6.8	6.7
$Zn(NO_3)_2$	94 8								208 9		
$ZnSO_4$					70.0	76.8		80.0	86.0	93.0	79.5

SOLUBILITY OF CANE SUGAR IN WATER

Grams of sugar in 100 grams of water, temperature in degrees Centigrade.

	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
$C_{12}H_{22}O_{11}$	179.2	190 5	203 9	219.5	238.1	260.4	287.3	320 5	363 1	415.7	487.2

Joliet Chemicals Inc.
Reference cited in
Patent No. 1,900,869
G.C. Connolly



51 UNITED STATES DISTRICT COURT.

* * (Caption—47-C-1098) * *

DEPOSITION OF GERALD C. CONNOLLY.

April 16, 1949.

52 Transcript of the deposition of Gerald C. Connolly, a witness produced on behalf of the defendant in the above entitled matter, taken by and before Louis Kabot, a Notary Public of the State of New Jersey, at the office of Lum, Fairlie & Foster, 605 Broad Street, Newark, New Jersey, on the 16th day of April, 1949, at ten o'clock in the forenoon, pursuant to Rules 26 and 30 of the Federal Rules of Civil Procedure and Notice of Oral Examination Before Trial served on the 5th day of April, 1949, hereto annexed.

Zimmerman & Norman, Esqs., By Harold W. Norman, Ecq., For the Plaintiff.

Schroeder, Merriam, Hofgren & Brady, Esqs., By John R. Allen, Esq., For the Defendants.

54 GERALD C. CONNOLLY, produced as a witness on behalf of the defendants, being duly sworn according to law by the Notary, testified as follows:

Direct Examination by Mr. Allen.

Q. Will you state your full name?
A. Gerald Charles Connolly.
Q. And where do you live?
A. Temporarily I am located at 1025 East Jersey Street, Elizabeth, New Jersey.
Q. What is your occupation?
A. Research Chemist for the Standard Oil Company of New Jersey.
Q. How long have you been there?
A. Twelve years.
Q. And prior to being with the Standard Oil of New Jersey, what was your occupation?
A. Well, I had been doing consulting research work for four years.

Q. And prior to that?

A. Before that I had been with the Silica Gel Corporation and the Davison Chemical Company, which was affiliated, for fourteen years.

Q. What years were those?

A. 1919 to 1933.

Q. What is your education?

A. I received my Ph.D. in Chemistry from Johns Hopkins University in 1916.

Q. Referring to the time when you went with Davison and Silica Gel in 1919, what were your duties?

55 A. Research.

Q. In what department?

A. The Silica Gel Corporation had not been brought into being as yet, and I was Research Chemist with the Davison Chemical Company, working on sulphuric acid and various other heavy chemicals.

Q. How long did that last?

A. That lasted for about a year and a half, when the Silica Gel Corporation was formed.

Q. Then what did you do?

A. I worked with the manufacture and use of gel adsorbents and catalysts for the next fourteen years.

Q. Were you familiar with the operation of the Silica Gel Plant?

A. Yes, I was.

Q. Will you state approximately when that plant was built?

A. Built in 1920 approximately.

Q. Will you describe rather briefly the nature of the plant?

A. They had two plants; this was the first one, and the second wasn't built until 1927. Do you want to go through the details of manufacture?

Q. Yes. I would like you to state what the plant was and how it operated.

A. Sodium silicate and sulphuric acid were mixed to form a hydrosol which in a period of a few hours set to the hydrogel. This was broken up into lumps of
56 one or two inches diameter, say, and then washed with water for a period of approximately 45 hours. The material was then dried at approximately 300 degrees F., forming the granular adsorbent. This was stored, and then when used was either ground or used as is, after a preliminary activation at an elevated temperature, usually

600 degrees F. for the granular material and approximately 1000 degrees F. for the powder material.

Q. Now, the process that you have described is the process of the first plant?

A. That is correct; also, the same procedure was used in the second plant .

Q. What kind of water was used in the wash?

A. When the plant was originally started we used well water, which was low in residue, and the temperature of this wash water was the temperature as it happened to come from the pipes. In other words, on a hot summer's day it was hotter than on a cold winer's day.

Q. Can you give us any idea as to the range of temperatures?

A. Well, I would say they ran from about 50 to 75; maybe more than that.

Q. What was done with the product that you have just discussed?

A. Most of the product in the early days went out in very small lots for experimental purposes, except the
57 powder material, which went out to an oil refining plant in Massachusetts, refining kerosene, in East Braintree, Massachusetts, if you want the full details.

Q. To whom did these other small quantities go?

A. Oh, they went to practically every company in the country .

Q. Were they given away?

A. No, they were sold.

Q. How long did you operate the plant in this manner?

A. Until approximately—I don't remember the exact date, but I would say just about the latter part of 1922 or the first of 1923.

Q. Then what changes were made?

A. At that time, based on preliminary work in the laboratory, we went into the use of water heated to prescribed temperatures for the purpose of controlling the pore sizes of the silica gel.

Q. Can you state the temperatures you used?

A. The temperatures we used were dependent on the application to which we were to put the gel. For overall general purposes we heated to between 150 up to, say, 175 degrees F. That's when we wanted wide pores. Where we wanted fine pores we washed down to temperatures of approximately 90 to 150 degrees F.

Q. Now, you commenced this when, did you say?
58 A. It would be just about the first of 1923; I would say within a month or two. It certainly was not later than the spring of 1923.

Q. And in the operation of the first plant were there any other changes made?

A. No; that was the major change.

Q. Referring to the product made originally, the first two years or so that the plant was in operation, was that product satisfactory?

A. No.

Q. Will you state why it wasn't satisfactory?

A. Well, the first thing was we used water of no definite temperature and the product was very ununiform; in other words, from one month to the next month it would be a different type product. The residue, that is, the salt content, was somewhat high and the porosity was too fine. So that the overall picture was that in repeated use where the material had to be regenerated, it simply lost efficiency too rapidly.

Q. Were these difficulties eliminated to a large extent when you changed the temperature of the wash water?

A. Yes.

Q. Will you state what experiments you made before these changes went into effect in the plant?

A. Well, the whole thing went back to the fact that we knew that the product wasn't satisfactory; that the
59 early product wasn't satisfactory. So I made experiments in the laboratory first on rewashing the dried silica gel. This improved the product but not sufficiently. Then I went to washing the hydrogel, first at a temperature of 150 degrees F. and later at lower and higher temperatures.

Q. And what was the purpose of these experiments?

A. The purpose of these experiments was to obtain a silica gel that would stand repeated regenerations and at the same time have a porosity that would meet the various uses or needs.

Q. Are you the Gerald C. Connolly who was one of the patentees of Patent No. 1900859 in the suit here?

A. That's right.

Q. With whom did you conduct these experiments about which you have just testified?

A. Do you mean the names of the men?

Q. Yes.

A. Well, there was a chap named A. F. Wurzbacher, J. B. Edmonds, W. L. Judefind; oh, maybe a couple more. Would that be enough of them?

Q. Well, I just want the persons with whom you did this work. They were the main ones?

A. They were the main ones.

Q. What was your position with the Silica Gel
60 Corporation during this period?

A. At that time I was what they called Head Research Chemist.

Q. Were you an officer of the company?

A. No, not then.

Q. Were you later?

A. Yes.

Q. What officer?

A. Vice President.

Q. Do you remember the capacity of this first plant?

A. I think it was just about 500 pounds per day, approximately.

Q. Was the plant in substantially continuous operation during this period?

A. Yes, it was in continuous operation.

Q. Mr. Connolly, I note that the application from which the patent was issued, Patent No. 1900859, was filed in 1930, but is stated to be a continuation in part of another application filed on December 30, 1927. Will you state why?

A. Yes. The reason that was that way; Watson, Coit, Morse and Grindle, they were our patent attorneys, and the case which they drew up, the first case that is, they did not appreciate the magnitude of the invention, and the second case was done to correct this error.

Q. It is my understanding from what you have just testified that you made this discovery or invention
61 back in 1922 or 1923.

A. That's right.

Q. And you put the process into operation in the plant in 1923?

A. That's right.

Q. The application wasn't filed until 1927?

A. That's right.

Q. Why is that?

A. We thought it was more important at the time to keep it a secret for the first four or five years. We hesitated a long time before we filed any application, and

the German firm, the IGF, were then busy making silica gel. The situation was so serious that we thought they might happen to bump into all this and beat us to the gun.

Q. Did you have a more or less standard temperature for the hot water wash or did it vary?

A. That tied up with the use; for example, in adsorbing vapors at low partial pressures and in a refrigerating cycle, we needed extremely fine pores. Therefore, we washed at a temperature of 90 to 105 degrees F. For a more or less universal gel we washed at a temperature of approximately 150 degrees F.

For catalytic purposes or for refining oils we washed at a temperature of approximately 175 degrees F. Of course, we washed at temperatures in between, we made some
62 at 125 degrees F., 165 degrees F. and various other temperatures, but those are the three key temperatures.

Q. What period are you talking about now?

A. That's the period from 1923 on, as long as I was with the Company and since. I undersand they use the same thing.

Q. I think you had better confine your answer to the time when you were with the Company.

A. That would be from 1923 to the middle of 1933.

Q. And the products you made under these varying temperatures of wash water, what was done with them?

A. Well, we used some for our own purposes and the rest were sold or put into plants which were then operating using silica gel .

Q. Do you remember the prices for which the products were sold?

A. Well, we attempted to tie up the silica gel with the purpose for which it was used; therefore, we put it out on a royalty basis. Where we actually sold the gel, well, we got a price from a dollar up.

Q. A dollar for what?

A. Per pound. The reason for this being the life of the material was very prolonged, and that it could be used over and oper again hundreds and hundreds of times.

Q. Are you familiar with the Patrick patent?

A. Yes, I am.

63 Q. No. 1297724?

A. Yes, that's right.

Q. Do you know Dr. Patrick?

A. Oh, yes.

Q. Was he working there with you?

A. No. Patrick had the position of a consultant for the Silica Gel Corporation and at the same time retained his position as Professor of Physical Chemistry at the Johns Hopkins University.

Q. He did consulting work with you then?

A. Yes, he accepted retainer's fees right along.

Q. What is the essential difference between your patent, the one in suit, and the Patrick patent?

A. Well, the Patrick patent covers the method we used up until the time in which we controlled the temperature of the wash water. In other words, this procedure we used the first two years in the operation of the Silica Gel Plant, but otherwise there is no essential difference. The point was, of course, that the product was ununiform, that is, the Patrick product was ununiform and unsatisfactory for use.

Q. And when did you say you started your expirements to improve the product that you originally made there at the plant?

A. I started that almost immediately. I would say early in 1921, but I didn't arrive at this method of controlling the temperature of the wash water until late
64 1922. I know that date very exactly because I happened to have been in England just previously, and it was after I came back I thought what we needed was a much better product and I was going to get it.

Mr. Allen: I think that is all.

Cross-Examination by Mr. Norman.

Q. Who laid out the first plant? Who designed it?

A. The first plant was an outgrowth of a small pilot plant that had been built in Astoria, New York, well, for the Government. I think it was for the Navy or Army—I have forgotten which—during the latter part of the War.

Q. And who built that pilot plant at Astoria?

A. Well, the Government financed it and a chap named Davis actually operated it.

Q. Did Mr. Patrick have anything to do with that?

A. Yes. The original idea was his.

Q. So the design of the plant incorporated his own ideas as to what was the best way to make silica gel?

A. That's right.

Q. When he came down to build this plant in—was it Baltimore or Curtis Bay?

A. Curtis Bay.

Q. (Continuation) Did that plant also incorporate his ideas as to the best way to make silica gel?

A. That's right.

65 Q. Was he in and out of the plant from time to time?

A. Yes.

Q. And familiar with the operation?

A. Oh, yes.

Q. Did he ever suggest to you that you could cure all these difficulties by a 90 to 105 degrees water wash?

A. Yes. He was just as much surprised as anybody by the fact that he could take a large piece of silica gel, that is, hydrogel, and shrink it.

Q. Are you familiar with the general nature of the specifications for silica gels put out by the Government for water vapor absorption capacity?

A. Yes.

Q. I have one in front of me dated May 8, 1945, bearing both Army Numbers and Navy Numbers, calling for Silica Gel Type 5, Grade A, having an absorptive capacity of 5.7 per cent of water at relative humidity of 10—are you familiar with that—and going on up to 80.

A. Yes, sir.

Q. If you didn't heat the wash water up to a temperature of 90 to 105 degrees what would be the effect as to your ability to meet these specifications?

A. Well, it is around 30 to 40 per cent relative humidity point that you get a definite hysteresis or flex in the absorption curve.

Q. Maybe you can explain that in the terms that 66 the Judge and I will understand ultimately.

A. Well, it is flexing of the curve from the smooth curve. In other words, it is a dip.

Q. And what is the effect in the absorptive capacity if you ever fail to heat the water to those temperatures?

A. You don't meet that specification.

Q. You don't absorb that quantity?

A. At that point.

Q. This specific list for Type 5, Grade A, 21½ per cent, at 40 per cent relative humidity, what would you absorb if you used water at well temperature of 50 degrees?

A. Well, I don't know exactly what it would be but it

would be considerably lower. I would say about four points.

Q. What would happen if you heated the water to boiling point, 212 degrees?

A. If you heat that high the pores would be too wide; in addition to that the structure would be too soft. In other words, it powders down on any violent agitation or shaking.

Q. What would be the effect on the absorptive capacity?

A. It wouldn't meet that point.

Q. Where would it fall down?

A. It would fall down on the whole front end of the absorptive curve. That is, I would say all the way from zero to 60 per cent relative humidity. In other words,
67 this could only be satisfactory for saturated vapors.

Q. Are these differences in absorptive capacity substantial or just nominal?

A. Oh, no; very substantial.

Mr. Norman: That is all.

Redirect Examination by Mr. Allen.

Q. What effect does hot water wash have on the speed with which the hydrogel is freed of salts?

A. It doesn't have as much influence as you expect. In other words, it is this; in a very short time, a few hours wash, when heating with hot or cold water, you can remove most of the salts and then the curve flattens out and you have a comparatively small amount of residue but still too high for a good absorbent. There is the necessity of maybe 36 hours of that washing.

Q. You are talking about washing at what temperature?

A. At any temperature.

Q. Isn't it generally known that you can get a faster wash with warmer water?

A. You can get a faster wash. As I say, it is very surprising. In other words, the laws of diffiusion enter here and you cannot accelerate it. In other words, the water has got to go in and wash these impurities out and you simply cannot force it too rapidly.

68 Q. But you knew all along that you could do it faster with an increase in temperature in the wash water, did you not?

A. Well, it is a little faster, yes, but not enough to be on economic point.

Q. What about the thoroughness of the wash?

A. The thoroughness of the wash? Well, what we attempted to do was to wash the material thoroughly throughout.

Q. Isn't it generally known that the warmer water will do a better and more complete wash job than cold water?

A. Yes, for ordinary washing purposes but I would say in this case diffusion enters into the picture and the full time that you get to wash the material down to the residue which we desire does not make very much difference. You just change the slope of your curve a little bit more.

Mr. Allen: That is all.

Recross Examination by Mr. Norman.

Q. Did you wash for the same length of time after you began using hot water as you had before?

A. Yes.

Q. 45 hours?

A. Approximately 45 hours. We had a little study on that, say, from 32 hours on up, and we all arrived at approximately 45 hours as answering our purposes.

Q. It isn't really a wash such as when you wash
69 clothes or wash your hands? There is no scrubbing action?

A. No, there is none.

Q. How does the wash take place mechanically?

A. You have a jelly structure which, after all, is semipermeable membranes. In other words, we find that there are definite laws of diffusion that are well known to any physical chemist; but the water has got to enter and remove these particles, salts or impurities, and the temperature effect is comparatively small.

Q. Well, silica gel or the hydrogel really just stands in water for awhile?

A. That's right.

Q. Then the impurities are absorbed out of that silica gel by the water, and you are gradually adding more water and gradually taking water away, are you not, rather slowly?

A. You are dealing with equilibriums. In other words, the materials, both inside and outside, have a tendency to

come to a definite equilibrium with the inside of the gel particle and the water outside the gel particle containing the same amount of salt.

Mr. Norman: That is all.

Gerald C. Connolly.

Subscribed and sworn to before me this 28th day of April, 1949.

Louis Kabot,
A Notary Public of New Jersey.

My commission expires 10/31/51.

71 UNITED STATES DISTRICT COURT.
• • (Caption—47-C-1098) • •

AFFIDAVIT OF J. R. MECREDY.

State of Maryland }
County of Baltimore } ss:

J. R. Mecredy, being first duly sworn, deposes and says:

I am of lawful age, a citizen of the United States, and reside in Towson, Maryland, at 510 W. Joppa Road.

I have been employed by The Davison Chemical Corporation since 1918 and am now manager of the Curtis Bay plant, which plant is engaged in the manufacture of silica gel.

I was familiar with the experiments conducted by Gerald C. Connolly and Ernest B. Miller in connection with the prosecution of their application for patent which resulted in the issuing of United States Patent No. 1,900,859 on March 7, 1933.

In the course of those experiments tests were run at the Curtis Bay plant of Silica Gel Corporation to determine the effect of using water heated to various degrees of temperature in controlling the apparent density of the silica gel and in the removal of impurities.

The principal impurity to be removed in the washing process is sodium sulphate. If the silica gel is not washed, the impurities will constitute about 40% of the dehydrated gel.

72 Substantially the same quantity of sodium sulphate can be removed by washing the gel at a given tempera-

ture, say 150°, for a period of forty-eight (48) hours as by washing the gel at a substantially lower temperature, say 80°, for eighty-four (84 hours. In each case these experiments demonstrated that the final product would have the same residue, that is the same quantity of impurities would have been removed, but the hot water washed gel would have a decidedly lower apparent density—the apparent density in the two cases being 0.58 and 0.72.

The following table shows effect of washing at various temperatures:

Temperature of wash water	Percent of Impurities removed	Density after activation at 600° F.
Room	98.7	0.75
105	99.4	0.696
150	99.7	0.606
175	99.7	0.522

Attached hereto and made a part hereof is a copy of government specifications for silica gels. It would be impossible to meet these specifications by washing the hydrogel at a temperature of below 90° F. or with water at a temperature of 200° F.

(Signed) J. R. Mecredy.

Subscribed and Sworn to before me this 22nd day of June, 1949.

(Signed) John Y. Davis.
Notary Public.

(Seal)

73 Jan-D-169

8 May 1945

Joint Army-Navy Specification
Desiccants (Activated)

Army Number	Navy Number
100-50	51D19

This specification was approved by the War Department and the Navy Department for use of procurement services of the Army and the Navy and supersedes the following specification:

U. S. Army	Navy Department
.....	51S32

1 March 1944

74 B. Types and Grades

B-1. Types.—Material covered by this specification shall be furnished in the following types as specified in the contract or order (see par. H-2):

Type II—Small particle size.
Type III—Medium particle size.
Type IV—Medium particle size with incorporated humidity indicator.
Type V—Ungraded.

B-2. Grades—Material shall be furnished in the following grades as specified in the contract or order (see par. H-2):

Grade A—High adsorption capacity.
Grade B—Medium adsorption capacity.
Grade C—Low adsorption capacity.

Grade D—Lowest adsorption capacity.

B-3. Types II and IV material shall be furnished in grade A only. Type III material shall be furnished in any of the grades as specified in the contract or order. (See par. H-2.) Type V material shall be furnished in grade A, B, or C as specified in the contract or order. (See par. H-2.)

Table I.—Water-vapor adsorption capacity

Relative humidity (percent)	Water-vapor adsorption, percent (minimum)					
	Type II	Type IV	Types III and V			Type III
	Grade A	Grade A	Grade A	Grade B	Grade C	Grade D
10	5.7	4.3	5.7	5.7	3.5	3.3
20	10.5	8.6	10.5	10.0	5.0	5.0
40	21.7	18.2	21.5	16.0	9.0	8.3
60	33.2	27.7	28.0	19.0	12.0	11.7
80	36.7	32.9	31.2	22.0	12.5	15.0

E-b. Indicating blended types.—Indicating blended types shall be not less than the capacities determined by an interpolation of the values shown in table I for the individual types comprising the blend.

E-4. Particle size (as shipped)—

E-4a. The particle sizes of the various types shall be as shown in table II. Unless otherwise specified, sieves shall conform to the requirements of Federal Specification RR-S-366.

75 UNITED STATES DISTRICT COURT.

* * (Caption—47-C-1098) * *

AFFIDAVIT OF WALTER A. PATRICK.

State of Maryland
County of Baltimore City } ss:

Walter A. Patrick, being first duly sworn, deposes and says:

I am of lawful age, a citizen of the United States, and reside in Baltimore, Maryland, at The Terraces, Mt. Washington.

I have been a professor of physical chemistry at Johns Hopkins University for the last twenty-five (25) years. I have made many inventions for which Letters Patent have been issued in my name. Several of such patents relate to the field of silica gels and among them is United States Patent No. 1,297,724, issued March 18, 1919.

Prior to the filing of my application, which resulted in the issuing of United States Patent No. 1,297,724, the removal of excess acid and salts formed in the manufacture

of silica gel was accomplished by dialysis. The invention of this patent was to permit the manufacture of silica gel without the use of a dialyzing membrane.

The statement in my patent, "if the wash water is heated, the washing of the gel is facilitated", was
76 incidental and no part of my invention. It was merely a statement of general principle. It so happens, however, that the salt which is to be removed by washing in this case is sodium sulphate which, unlike most other salts, actually has a lower solubility at 100° C. than at room temperature at 20° C.

At the time of my application, which resulted in the issuance of United States Patent No. 1,297,724, I washed silica hydrogel with unheated tap water.

I designed a pilot silica gel plant which was built in Astoria, New York, in 1918 for the Government of the United States. In that plant the water for washing the silica hydrogel was used at whatever temperature the water came out of the tap. I also participated in the design of the first plant built for Silica Gel Corporation at Curtis Bay about 1920. The water used in washing the silica hydrogel at that plant was at the temperature at which the unheated water was supplied, varying from about 50° to about 75° F.

It was not until after the invention of Gerald C. Connolly and Ernest B. Miller, which resulted in United States Patent No. 1,900,859, issued March 7, 1933, that I had any idea that there was any relationship between the apparent density of the gel and the temperature of the wash water used.

(Signed) Walter A. Patrick.

Subscribed and Sworn to before me this 22nd day of June, 1949.

(Signed) John F. Donnelly,
(Seal) *Notary Public.*

77 UNITED STATES DISTRICT COURT.
* * (Caption—47-C-1098) * *

ORDER.

This cause coming on to be heard on Motion of Defendants for Summary Judgment dismissing the complaint on the ground that the claims of the remaining patent in suit Connolly et al. No. 1,900,859 are invalid in view of Patrick patent No. 1,297,724 of May 18, 1919 and the Court having heard the arguments of counsel, having read and considered the briefs and affidavits submitted by the parties, the file history of the patent in suit and the deposition of Gerald C. Connolly and being fully advised in the premises:

It Is Hereby Ordered:

1. That the Connolly et al. patent in suit No. 1,900,859 is invalid for want of invention and the complaint herein is hereby dismissed.
2. The Court retains jurisdiction of the case with respect to the issues presented by the counterclaim.
3. The matter of costs (including attorneys' fees) is deferred pending disposition of the counterclaim.

Enter:

Elwyn R. Shaw.
Judge.

Approved as to form:
Zimmerman and Norman,
Attorneys for Plaintiff.
Schroeder, Merriam, Hofgren & Brady,
Attorneys for Defendants.

June 29, 1949.

78 UNITED STATES DISTRICT COURT.
* * (Caption—47-C-1098) * *

ORDER.

This cause coming on to be heard on Motion of Defendants for Summary Judgment dismissing the complaint on the ground that the claims of the remaining patent in suit Connolly et al. No. 1,900,859 are invalid in view of Patrick patent No. 1,297,724 of May 18, 1919, and the Court having heard the arguments of counsel, having read and considered the briefs and affidavits submitted by the parties, the file history of the patent in suit and the deposition of Gerald C. Connolly and being fully advised in the premises:

It Is Hereby Ordered:

1. That the Connolly et al. patent in suit No. 1,900,859 is invalid for want of invention, that the complaint herein is hereby dismissed, that judgment be entered on the complaint filed herein for the defendants and against the plaintiff, and that plaintiff take nothing by its action herein.

2. The Court retains jurisdiction of the case with respect to the issues presented by the counterclaim.

3. The matter of costs (including attorneys' fees) is deferred pending disposition of the counterclaim.

Enter:

LaBuy.

Approved as to form:

Zimmerman & Norman,
Attorneys for Plaintiff.

Schroeder, Merriam, Hofgren & Brady,
Attorneys for Defendants.

July 26, 1949.

79 UNITED STATES DISTRICT COURT,

Northern District of Illinois,

Eastern Division.

The Davison Chemical Corporation, a corporation, *Plaintiff,* *vs.* Joliet Chemicals, Inc., a corporation, Desplaines Oil Company, a corporation, Joliet Chemicals, Ltd., a partnership, and Kenneth F. Nash, *Defendants.*	Civil Action No. 47 C 1098.

NOTICE OF APPEAL.

Notice is hereby given that The Davison Chemical Corporation, a corporation, the plaintiff above named, hereby appeals to the Court of Appeals for the Seventh Circuit from that part of the order entered on June 29, 1949, ordering that the Connolly et al., patent in suit No. 1,900,859 is invalid for want of invention and that the complaint herein is hereby dismissed, and from that part of the order entered July 26, 1949, ordering that the Connolly et al., patent in suit No. 1,900,859 is invalid for want of invention; that the complaint herein is hereby dismissed; that judgment be entered on the complaint filed herein for the defendants and against the plaintiff; and that plaintiff take nothing by its action herein.

(Sgd.) Harold W. Norman,
Attorney for Plaintiff,
111 W. Monroe Street,
Chicago, Illinois.

Filed July 27, 1949.

81 United States of America,
Northern District of Illinois. } ss:

I, Roy H. Johnson, Clerk of the United States District Court for the Northern District of Illinois, do hereby certify the above and foregoing to be the Original Agreed Statement of Case under Rule 76 approved by said Court and filed in the Clerk's office thereof, on the 4th day of August, 1949, and is The Record on Appeal.

In Testimony Whereof, I have hereunto subscribed my name and affixed the seal of the aforesaid Court at Chicago, this 23rd day of August, 1949.

Roy H. Johnson,
Clerk.

82 UNITED STATES COURT OF APPEALS

For the Seventh Circuit.

The Davison Chemical Corporation, a corporation, *Plaintiff-Appellant,* *vs.* Joliet Chemicals, Inc., a corporation, Desplaines Oil Company, a corporation, Joliet Chemicals, Ltd., a partnership, and Kenneth F. Nash, *Defendants-Appellees.*	Civil Action No. 9991.

STIPULATION FOR PRINTING OF RECORD.

(Filed Aug. 24, 1949. Kenneth J. Carrick, Clerk.)

It is hereby stipulated between counsel for appellant and counsel for appellees that the printed record shall consist of the entire agreed statement of case under Rule 76 and copies attached thereto, with the exception of the Government specifications for silica gels attached to the affidavit of J. R. Mecready entitled "Joint Army-Navy Specification Desiccants (Activated)". Only the following portions of said Government specifications shall be printed:

1. That portion of page 1 prior to Section A.
2. All of Section B on page 2.
3. All of Table I on page 3.

Harold W. Norman,

Attorney for Plaintiff-Appellant,

Schroeder, Merriam Hofgren & Brady,
Attorneys for Defendants-Appellees.

UNITED STATES COURT OF APPEALS

For the Seventh Circuit,

Chicago 10, Illinois.

I, Kenneth J. Carrick, Clerk of the United States Court of Appeals for the Seventh Circuit, do hereby certify that the foregoing printed pages contain a true copy of the printed transcript of record, filed November 14, 1949, in:

Cause No. 9991.

The Davison Chemical Corporation,
Plaintiff-Appellant,

vs.

Joliet Chemicals, Inc., *et al.*,
Defendants-Appellees,

as the same remains upon the files and records of the United States Court of Appeals for the Seventh Circuit.

In Testimony Whereof I hereunto subscribe my name and affix the seal of said United States Court of Appeals for the Seventh Circuit, at the City of Chicago, this 23rd day of May, A. D. 1950.

Kenneth J. Carrick,
(Seal) *Clerk of the United States Court of Appeals for the Seventh Circuit.*

At a regular term of the United States Court of Appeals for the Seventh Circuit, held in the City of Chicago and begun on the fifth day of October, in the year of our Lord one thousand, nine hundred and forty-eight, and of our Independence the one hundred seventy-third.

The Davison Chemical Corporation, *Plaintiff-Appellant,* 9991 *vs.* Joliet Chemicals, Inc., Des Plaines Oil Company, Joliet Chemicals, Ltd., and Kenneth F. Nash, *Defendants-Appellees.*	Appeal from the United States District Court for the Northern District of Illinois, Eastern Division.

And afterward, to-wit, on the twenty-fifth day of August, 1949, there was filed in the office of the Clerk of this Court an appearance for the appellant, which said appearance is in the words and figures following, to-wit:

UNITED STATES COURT OF APPEALS

For the Seventh Circuit.

Cause No. 9991.

The Davison Chemical Company,
Plaintiff-Appellant,

vs.

Joliet Chemicals, Inc., *et al.*,
Defendants-Appellees.

The Clerk will enter my appearance as counsel for plaintiff-appellant.

Harold W. Norman,
111 W. Monroe Street,
Chicago, Illinois.

Endorsed: Filed Aug. 25, 1949. Kenneth J. Carrick, Clerk.

And afterward, to-wit, on the ninth day of December, 1949, there was filed in the office of the Clerk of this Court an appearance for the appellees, which said appearance is in the words and figures following, to-wit:

UNITED STATES COURT OF APPEALS

For the Seventh Circuit.

Cause No. 9991.

Davison Chemical Corp.,
Plaintiff-Appellant,

vs.

Joliet Chemicals, Inc., *et al.*,
Defendants-Appellees.

The Clerk will enter our appearance as counsel for Appellees.

John Rex Allen,
2200 Opera Bldg.

Jules L. Brady,
2200 Opera Bldg.

Endorsed: Filed Dec. 9, 1949. Kenneth J. Carrick, Clerk.

And afterward, to-wit, on the thirty-first day of January, 1950, the following further proceedings were had and entered of record, to-wit:

UNITED STATES COURT OF APPEALS

For the Seventh Circuit,

Chicago 10, Illinois.

January 31, 1950.

Before:

Hon. J. Earl Major, Chief Judge.
Hon. Philip J. Finnegan, Circuit Judge.
Hon. Walter C. Lindley, Circuit Judge.

The Davison Chemical Corporation, *Plaintiff-Appellant,* 9991 *vs.* Joliet Chemicals, Inc., Des Plaines Oil Company, Joliet Chemicals, Ltd., and Kenneth F. Nash, *Defendants-Appellees.*	Appeal from the United States District Court for the Northern District of Illinois, Eastern Division.

Now this day come the parties by their counsel, and this cause comes on to be heard on the transcript of the record and the briefs of counsel and on oral argument by Mr. Harold W. Norman, counsel for the appellant, and by Mr. John Rex Allen, counsel for the appellees, and the Court takes this matter under advisement.

And afterward, to-wit, on the eighth day of February, 1950, there was filed in the office of the Clerk of this Court the opinion of the Court, which said opinion is in the words and figures following, to-wit:

IN THE UNITED STATES COURT OF APPEALS

For the Seventh Circuit.

No. 9991. October Term, 1949, January Session, 1950.

The Davison Chemical Corporation, *Plaintiff-Appellant*, *vs.* Joliet Chemicals, Inc., Des Plaines Oil Company, Joliet Chemicals, Ltd., and Kenneth F. Nash, *Defendants-Appellees.*

Appeal from the United States District Court for the Northern District of Illinois, Eastern Division.

February 8, 1950.

Before MAJOR, *Chief Judge*, FINNEGAN and LINDLEY, *Circuit Judges.*

LINDLEY, *Circuit Judge.* In plaintiff's suit to enjoin infringement of patent No. 1,900,859 to Connolly *et al.*, March 7, 1933, covering a process for making silica gel, the court, upon motion for summary judgment, having before it the Connolly patent, its file wrapper, prior patent No. 1,297,724 to Patrick, March 18, 1919, the deposition of Connolly, the affidavits of Mecredy and Patrick as to the status of the prior art, not disputed by plaintiff or defendants, allowed the motion, holding the Connolly patent invalid for want of invention and dismissing the complaint. From that judgment, plaintiff appeals.

Silica gel is a hard, transparent substance with ultramicroscopic pores, possessing ability to adsorb moisture from the air, making it useful as a desiccant. It has other commercial uses where adsorptive purposes are desired and where catalysts are useful, as in oil refining. Some

commercial uses necessitate very small pores in the physical structure while for certain others, larger pores are desirable. All this was common knowledge when Connolly applied for his patent. The industry was then manufacturing silica gel by mixing sodium silicate with an acid under violent agitation, allowing the resulting product to set, breaking it into small pieces, washing it free from acid and salt and drying it at a fixed temperature. Nothing appeared in the prior art, however, as to the desirability of controlling the temperature of the water in which the material was washed except that Patrick had asserted that "hot water" was preferable.

Patrick had described the process and received his patent therefor. In his claims he prescribed washing but made no reference to the temperature of the water. His only reference to that matter appeared in his description where he expressed his preference for hot water without giving reasons.

It seems clear that Connolly discovered for the first time that a definite relationship exists between the temperature of the wash water and the porosity of the final product. He found and announced that the higher the temperature, the lower the density. This scientific fact, apparently, no other delver in the art had discovered; therein lies the difference between the two patents. In other words, Connolly adopted the process of Patrick but claimed an improvement "pertaining to controlling the apparent density of the gel which comprises adjusting the temperature of the heated water, the temperature chosen for the water being the higher as the apparent density desired is lower"; or, as stated in Claim 7, "that improvement relating to controlling the apparent density of the gel within the range of about 0.52 to 0.79 when activated at about 600° to 1600° F., which comprises, adjusting the temperature of the wash water within the range of about 160° to 190° F., the temperature chosen for the water being the higher as the apparent density desired is lower." The process was old. The washing was old. The specific suggestion of Connolly in his claimed improvement that the higher the temperature of the wash water, the lower the density of the final product was new. It follows, we think, that Patrick did not anticipate Connolly's specific teaching; thus the question before us is whether that teaching amounts to invention.

It is one thing of course to discover a scientific fact,

a law existing in nature, and quite another to invent a means of making that discovery useful. One may well know of the physical power of leverage and that it may be achieved by divers mechanical means, including the simple lever, transmission of power from a larger gear wheel to a smaller one and the transfer of power from a larger pulley to a smaller one, but the decision as to whether invention grows out of a means devised to utilize such physical quality or scientific fact or law of nature, whatever term one may use, is the same as that involved in every case questioning invention and that is whether the patentee has taught something which, within the patent statute, amounts to patentable invention. Consequently the question becomes one of whether, when Connolly discovered the scientific fact that temperature of the washing water directly affects the density of the washed product, he then devised a process for utilization of that scientific fact which amounted to invention. What the skilled scientist, having been informed of the newly discovered scientific fact, would have done, would amount only to the exercise of ordinary skill in his profession. Knowing that the porosity and density of the gel varies directly in relation to the temperature of the rinsing water, was it invention for Connolly to apply the law of nature as he did?

While a scientific truth, or its mathematical expression is not patentable invention, a novel and useful structure created with the aid of knowledge of scientific truth may be. *Mackay Co.* v. *Radio Corp.*, 306 U. S. 86 at 94. He who discovers a hitherto unknown scientific fact or law of nature has no claim to a monopoly of it; if there is to be invention from such a discovery it must come from the application of the law of nature or scientific fact to a new and useful end. *Funk Brothers Seed Company* v. *Kalo Inoculant Company*, 333 U. S. 127. See also *De Forest Radio Company* v. *General Electric Company*, 283 U. S. 664, 685; *Wall* v. *Leck*, 66 Fed. 552, 555 (C. A. 9); *In re Modine*, 57 F. 2d 355, 356. Discovery of a previously unknown law of operation, involved in no new method, has never been held to be invention. The application of the law must be novel nad inventive in character. *Luten* v. *Whittier*, 251 F. 590; *General Electric* v. *Cooper Hewitt Electric*, 249 F. 69 (C. A. 6).

Keeping these principles in mind and applying them to the present case, we assume that Connolly discovered that the temperature of the wash water determined the

pore size and, therefore, the specific gravity or density of the gel but, we think, that, once having discovered this, it required nothing more than the ordinary skill of the scientist to determine that maintaining the temperature of the water at a constant point would make the size of the pore, and the density of the silica gel, uniform.

In other words the artisan, knowing that the temperature determines the porosity, could very readily, by empirical methods, determine the particular pore size required for a particular use of the gel and then, by maintaining the wash water at the temperature at which such pore size was attained, procure the uniform product desired. Stated otherwise, it seems to us that Connolly merely transferred to paper his discovery of a scientific fact which, when discovered, was sufficient to enable any skilled artisan to accomplish what he achieved. "To find the range, required nothing more than routine experimentation by a skilled chemist, and that being so, invention was not involved." *American Lecithin Co. v. Warfield Co.*, 128 F. 2d 522, 526 (C. A. 7). See also *Nivocol Chemical Mfg. Co., Inc.* v. *Powers & Anderson Dental Co., Inc.*, 128 F. 2d 904 (C. A. 4). We agree, therefore, that the patent to Connolly is invalid.

Plaintiff insists that the court wrongfully entered summary judgment. Rule 56(c) of Civil Procedure permits such a motion to be entertained "if the pleadings, depositions and admissions on file, together with affidavits, if any, show that there is no genuine issue as to any material fact and that the movingparty is entitled to a judgment as a matter of law." Plaintiff's contention in this respect, therefore, must stand or fall upon our determination of whether there remained in reality, "a genuine issue as to any material fact."

Defendants' motion necessarily admitted all averments of plaintiff's complaint well pleaded. Insofar as the validity of the patent involved is concerned, they pleaded, as prior art defense, only the Patrick patent. There are in the record the deposition of Connolly himself, two affidavits and the file wrapper. From them the facts that we have related appear without contradiction; that is to say, it appears that everything was old except Connolly's discovery and his application of that discovery to the process described in his patent for an improvement over the prior art. His prescription for that process, we have held, did not constitute invention. We are unable to find remaining any genuine issue of fact between plaintiff and

defendants. Consequently, the court rightfully allowed the motion for summary judgment. Such practice in similar cases is not new. *Gatch Wire Goods Co.* v. *W. A. Laidlaw Wire Co., et al.,* 108 F. 2d 433 (C. A. 7); *Milcor Steel Company* v. *George A. Fuller Company,* 316 U. S. 143, 144; *Allen, et al.* v. *Radio Corporation of America,* 47 F. Supp. 244; *Luten* v. *Kansas City Bridge Co.,* 272 F. 533; *Juniper Mills, Inc.* v. *J. W. Landenberger & Co.,* 6 F. R. D. 463.

THE JUDGMENT IS AFFIRMED.

And on the same day, to-wit, on the eighth day of February, 1950, the following further proceedings were had and entered of record, to-wit:

UNITED STATES COURT OF APPEALS

For the Seventh Circuit,

Chicago 10, Illinois.

Wednesday, February 8, 1950.

Before:

Hon. J. Earl Major, Chief Judge.
Hon. Philip J. Finnegan, Circuit Judge.
Hon. Walter C. Lindley, Circuit Judge.

The Davison Chemical Corporation, *Plaintiff-Appellant,* vs. Joliet Chemicals, Inc., Des Plaines Oil Company, Joliet Chemicals, Ltd., and Kenneth F. Nash, *Defendants-Appellees.*	Appeal from the United States District Court for the Northern District of Illinois, Eastern Division.

9991

This cause came on to be heard on the transcript of the record from the United States District Court for the Northern District of Illinois, Eastern Division, and was argued by counsel.

On consideration whereof, it is ordered and adjudged by this Court that the judgment of the said District Court in this cause appealed from be, and the same is hereby, Affirmed, with costs.

And afterward, to-wit, on the twenty-third day of February, 1950, there was filed in the office of the Clerk of this Court a petition for rehearing, which said petition is in the words and figures following, to-wit:

In the

United States Court of Appeals

For the Seventh Circuit

No. 9991

THE DAVISON CHEMICAL CORPORATION, *Plaintiff-Appellant,* *vs.* JOLIET CHEMICALS, INC., DES PLAINES OIL COMPANY, JOLIET CHEMICALS, LTD., and KENNETH F. NASH, *Defendants-Appellees.*	Appeal from the United States District Court for the Northern District of Illinois, Eastern Division.

U. S. C. A.-7
FILED
FEB 23 1950
KENNETH J. CARROCK
CLERK

PETITION FOR REHEARING.

EDWARD A. ZIMMERMAN,
HAROLD W. NORMAN,
Attorneys for Plaintiff-Appellant.

THE BUNTHORP-WARREN PRINTING COMPANY, 210 WEST JACKSON, CHICAGO

List of Authorities Cited.

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